POLYMER DATA HANDBOOK

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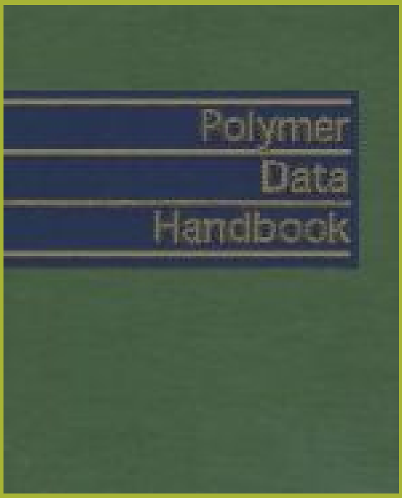

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EDITED BY JAMES E. MARK, UNIVERSITY OF CINCINNATI

PUBLISHED BY OXFORD UNIVERSITY PRESS

The online version of the *Polymer Data Handbook* includes key data on over two hundred polymers. Please note that entries are presented as PDF files and can only be read using Adobe Acrobat Reader Version 3. If you do not have the freeware reader, it can be downloaded from Adobe in the United States or Adobe in the United Kingdom. Each entry opens with a citation of the contributor's name and notations of acronyms and trade names, class of polymer, structure, and major applications. These are followed by tabular displays showing the properties of each polymer. The maximum consistency possible has been established for properties presented with regard to format, terminology, notations, and units. However, not all properties are applicable to all polymers contained in the handbook; some properties may not even be relevant for certain polymer classes. Also, some polymers exhibit properties shown by few others (e.g., electroluminescence); these properties have been noted as "Properties of Special Interest." Each entry closes with a list of references for the reader interested in further investigation of a polymer.

View the editor's preface to the print edition (HTML format).

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PREFACE TO THE PRINT EDITION

The *Polymer Data Handbook* offers, in a standardized and readily accessible tabular format, concise information on the syntheses, structures, properties, and applications of the most important polymeric materials. Those included are currently in industrial use or they are under study for potential new applications in industry and in academic laboratories. Considerable thought was given to the criteria for selecting the polymers included in this volume. The first criterion was current commercial importance—the use of the polymer in commercial materials—for example, as a thermoplastic, a thermoset, or an elastomer. The second criterion was novel applications—a polymer that is promising for one or more purposes but not yet of commercial importance—for example, because of its electrical conductivities, its nonlinear optical properties, or its suitability as a preceramic polymer. The hope is that some readers will become interested enough in these newer materials to contribute to their further development and characterization. Finally, the handbook includes some polymers simply because they are unusually interesting—for example, those utilized in fundamental studies of the effects of chain stiffness, self-assembly, or biochemical processes.

Based on these three criteria, more than two hundred polymers were chosen for inclusion in this work. The properties presented for each polymer include some of great current interest, such as surface and interfacial properties, pyrolyzability, electrical conductivity, nonlinear optical properties, and electroluminescence. Not all the properties are available for all the polymers included, and some properties may not even be relevant for certain polymer classes. Some polymers exhibit properties shown by few others—such as electroluminescence—and those have been presented as "Properties of Special Interest."

The handbook entries were written by authors carefully chosen for their recognized expertise in their specific polymers. The authors were asked to be highly selective, to choose and document those results that they considered to have the highest relevance and reliability. All the entries were then reviewed carefully by one or more referees, to ensure the highest quality and significance. Care was taken to achieve maximum consistency between entries, especially with regard to terminology, notations, and units. The goal was to facilitate searches in the printed version of the handbook and electronically on the online site.

Grateful acknowledgment is made here to the important contributions of the anonymous referees. It is also my real pleasure to thank a number of people at Oxford University Press for their help: specifically, Robert L. Rogers and Sean Pidgeon contributed greatly to the initiation and formulation of the basic structure of the handbook, and Matthew Giarratano carried out its implementation. It is appropriate here to thank my wife Helen for the kind of support, tangible and intangible, that makes an intimidating project, like this one, doable and sometimes even a pleasant experience.

James E. Mark
University of Cincinnati
October 1998

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Duradene

Durez

Duroflex

Eastoflex

Ebonite

EC

Ekonol

Elastic, plastic, and hydrogel-forming protein-based polymers

Elastic protein-based polymers

Elastomeric polyethylene (very highly branched)

Elastomeric poly(phosphazene)

Elastomeric polypropylene (stereoblock)

Electrically conductive polymer

elPP

ELPP

Elvanol

Elvax

Emeraldine

Engineering thermoplastics

- Poly(amide imide)
- Poly(2,6-dimethyl-1,4-phenylene oxide)
- Poly(ether imide)
- Poly(methylene oxide)

EP

EPDM

EPDM rubber derivative

Epi-Cure

Epikote

Epi-Res

EPM

Epon

Epotuf

Epoxy resins

EPR (as copolymer)

Ethene- propene-diene elastomers

Ethylcellulose

Ethylene copolymer

Ethylene copolymer, homogeneous

Ethylene copolymer, ultra-low-density

Ethylene-propylene-diene monomer elastomers

Ethylene-vinyl acetate copolymer

Ethylene-vinyl alcohol copolymer

EVA

Ethylene-vinyl acetate copolymer

Ethylene-vinyl alcohol copolymer

Eval

EYPEL-F

Fenilin

Fibroin

Flemion

Flexible linear aliphatic polyester

Flexible linear aromatic polyester

Floraflon

Fluon

Fluorel

Fluoroelastomer

Fluoroplast

Fluorosilicone

Fortron

FOx

FS

Fullerene-containing polymers

Gantrez M

Gelatin

Gelvatol

Gentro

Geon

GL

Glaskyd

Glass resin

- Poly(methylsilsesquioxane)
- Poly(phenylsilsesquioxane)

Glycogen

Gohsenol

Good-ritel

Grilamid

GR-M

Gutta percha

Halobutyl rubber

Halon

p-Halostyrene

HBPSE

HDPE

Hetron

Hevea

H-H polystyrene

H-H PS

H-H PVC

HH PVC

High-density linear polyethylene

High-performance polymer

High-pressure PE

Homogeneous ethylene copolymers

Homopolymers

- Poly(N-vinyl carbazole)
- Poly(4-vinyl pyridine)
- Poly(N-vinyl pyrrolidone)

Hostaflon

HPC

HPCS

HPZ

HSQ

Humex

Hycar

Hydridopolycarbosilane

Hydridopolysilazane

Hydridosilsesquioxane

Hydrogel-forming protein-based polymers

Hydrogen silsesquioxane

Hydron

Hydroxypropylcellulose

IIR

In-chain modified polysiloxane

Inorganic and semi-inorganic polymers

- Poly[(*n*-butylamino)thionylphosphazene]
- Poly(dimethylferrocenylethylene)
- Poly(ferrocenyldimethylsilane)
- Polygermanes
- Polymeric selenium
- Polymeric sulfur
- Polyphosphates

- Poly(phosphonate)
- Poly(sulfur nitride)
- Poly(vinylferrocene)

IR

Isobutylene isoprene rubber

Isotactic polypropylene

JSR

- Acrylonitrile-butadiene elastomers
- Styrene-butadiene elastomers

Kadel

Kapton

Kel-F 81

Kevlar

KF

Kollidon

Kraton D1100 SBS

Kraton G1600 SEBS

Krynac

Kynar

Ladder coat

LDPE

Leucoemeraldine

Levapren

Levasint

Lexan

Linear aliphatic flexible polyester

Linear aromatic polyester

Linear aromatic rigid polyester

Linear flexible aromatic polyester

Linear high-density polyethylene

Linear low-density polyethylene

Linear low-density polyethylene, metallocene

Linear styrene-butadiene-styrene triblock copolymer

Linear styrene-(ethylene-butylene)-styrene triblock copolymer

LLDPE

LLDPE, single site catalyzed

Low-density linear metallocene polyethylene

Low-density linear polyethylene

Low-density polyethylene

Low-pressure PE

Low swell

LPE

LPHSQ

LS

Lucite

Lustran

Lutonal M

Luvican

Luviskol

Makrolon

Maranyl

Melamines

Metallocene linear low-density polyethylene

Metallocene PE

Metallophthalocyanine polymers

Methylphenyl silicone oil

Methylsilicone oil

Methyl-T

Microthene

mLLDPE

MN

Modic

Molecular bracelet

Molecular necklace

Movital

Mowiol

4MS

p-MS

MST

Nafion

Natsyn

Natural rubber

NBR

Neoflon

Neoprene

Nipol

Acrylonitrile-butadiene elastomers

Styrene-butadiene elastomers

NK

Nomex

Norsorex

Novatec

Novolacs

NR

N-substituted 1-nylons

Poly(*n*-butyl isocyanate)

Poly(*n*-hexyl isocyanate)

Nylatron

Nylon 2

Nylon 3

Nylon 4,6

Nylon 6

Nylon 6 copolymer

Nylon 6,6

Nylon 6,6 copolymer

Nylon 6/6T

Nylon 6,10

Nylon-610

Nylon 6,12

Nylon 11

Nylon 12

Nylon MXD6

Nysyn

OCF

ODA-PMDA

PA-6

PA-11

PA 12

PA 610

PA-610

PAA

PAAc

PAAm

PAI

PAMAM dendrons and dendrimers

PAMS

PANI

Paracril

Parylene N

PATP

PB

PBA

PBD

PBFP

PBI

PBIC

PBLG

PBO

PBT

Poly(benzobisthiazole)

Poly(butylene terephthalate)

PBTFP

PBZI

PBZT

PC

Polycarbonate

Poly(methylsilmethylene)

PCHMA

PCL

PCS

Poly(*p*-chlorostyrene)

Poly(methylsilmethylene)

PCTFE

PDBuS

PDES

PDHeS

PDHS

PDMS

Poly(dimethylsiloxane)

Poly(dimethylsilylene)

PDMS, cyclic

PDPeS

PDPrS

PDPS

PDX

PDXL

PDXP

PE

PE, branched

PE, high-pressure

PE, low-pressure

PEA

PECH

Pedigree

PEEK

PEI

Poly(ether imide)

Poly(ethylene imine)

PEK

PEN

PEO

Perbunan C

Peregal

Perfluorinated ionomers

Pernigraniline

PES

Poly(ether sulfone)

Poly(ethylene sulfide)

PET

PF

PFPN

PGA

PHB

P(3HB)

PHBA

PHE

PHEMA

Phenolic resins

Phenyl silicobenzoic anhydride

Phenyl siliconic anhydride

Phenyl-T

PHEX

PHIC

PIB

Pioester

cis -PIP

trans-PIP

PLA

Plasdone

Plaskon

Plastic protein-based polymers

Plexiglas

Plioflex

Pliolite

PLOS

PMA

- Poly(methacrylic acid)
- Poly(methyl acrylate)

PMAA

PMAN

PMBD

PMDA-ODA

P*p*MeS

PpMeS

PMMA

PMP

P4MPE

PMPS

- Poly(methylphenylsiloxane)
- Poly(methylphenylsilylene)

PMS

P(alpha)MS

P*p*MS

P-*p*MS

P4MS

PMSQ

PNF elastomer

PNIPA

PNIPAAm

POE

Polyacetals

- Polychloral
- Poly(1,3-dioxolane)
- Poly(methylene oxide)

Polyacetylene

Polyacrylamide

Poly(acrylic acid)

Poly(acrylonitrile)

Poly(L-alanine)

Poly(aldehyde)

Polyamide 12

Poly(amide imide)

Polyamides, aliphatic

- Nylon 3
- Nylon 4,6
- Nylon 6
- Nylon 6 copolymer
- Nylon 6,6
- Nylon 6,10
- Nylon 6,12
- Nylon 11
- Nylon 12
- Nylon MXD6

Polyamides, aromatic

- Kevlar
- Nylon 6,6 copolymer

- Poly(*p*-benzamide)
- Poly(*m*-phenylene isophthalamide)

Poly(amidoamine) dendrimers

Polyamine

Polyanhydrides

- Poly(1,3-bis-*p*-carboxyphenoxypropane anhydride)
- Poly(erucic acid dimer anhydride)

Polyaniline

Polyaramid

Polyaramide

Polyaromatics

- Poly(1,4-phenylene)
- Poly(1,4-phenylene vinylene)
- Polyquinoline
- Poly(*p*-xylylene)

Poly(aryloxy)thionylphosphazenes

Poly(*p*-benzamide)

Poly(benzimidazole)

Poly(benzobisoxazole)

Poly[(benzo[1,2-d:5,4-d']bisoxazole-2,6-diyl)-1,4-phenylene]

Poly(benzobisthiazole)

Poly[(benzo[1,2-d:4,5-d']bisthiazole-2,6-diyl)-1,4-phenylene]

Poly(gamma-benzyl-L-glutamate)

Poly(1,3-bis-*p*-carboxyphenoxypropane anhydride)

Poly(bis maleimide)

Polybutadiene

1,2-Polybutadiene

cis-1,4-Polybutadiene

trans-1,4-Polybutadiene

1,2-Polybutadiene

cis-1,4-Polybutadiene

trans-1,4-Polybutadiene

Polybutene

Poly(butene-1)

Poly[(*n*-butylamino)thionylphosphazene]

Polybutylene

Poly(butylene terephthalate)

Poly(*n*-butyl isocyanate)

Poly-(epsilon)-caproamide

Poly(epsilon-caprolactone)

Polycarbonate

Polycarbonate, bisphenol-A

Polycarbosilanes

Poly(methylsilmethylene)

Poly(silylenemethylene)

Polychloral

Poly(2-chloro-1,3-butadiene)

Poly(1-chloro-1-butenylene)

Polychloroprene

Poly(*p*-chlorostyrene)

Poly(chlorotrifluoroethylene)

Polyclar

Poly(CPP)

Poly(CPP-SA)

Poly(cyclohexyl methacrylate)

Poly(1,3-cyclopentylenevinylene)

Poly(di-*n*-butylsiloxane)

Poly(diethylsiloxane)

Polydi-*n*-hexylsilane

Poly(di-*n*-hexylsiloxane)

Poly(di-*n*-hexylsilylene)

Poly(dimethylferrocenylethylene)

Poly(2,6-dimethyl-1,4-phenylene oxide)

Polydimethylsilane

Poly(dimethylsiloxane)

Poly(dimethylsiloxanes), cyclic

Poly(dimethylsilylene)

Poly(dimethylsilylene-*co*-phenylmethylsilylene)

Poly(1,3-dimethyl-2,2,4,4-tetramethylcyclodisilazane)

Poly(1,3-dioxepane)

Poly(1,3-dioxolane)

Poly(di-*n*-pentylsiloxane)

Poly(diphenylsiloxane)

Poly(di-*n*-propylsiloxane)

Polydodecanolactam

Poly(EAD)

Poly(EAD-SA)

Poly(epichlorohydrin)

Poly(erucic acid dimer anhydride)

Polyesters

- Poly(butylene terephthalate)
- Poly(epsilon-caprolactone)
- Polycarbonate
- Polyesters, unsaturated
- Poly(ethylene-2,6-naphthalate)

- Poly(ethylene terephthalate)
- Poly(glycolic acid)
- Poly(4-hydroxy benzoic acid)
- Poly(hydroxybutyrate)
- Poly(lactic acid)

Polyesters, aliphatic

- Poly(epsilon-caprolactone)
- Poly(hydroxybutyrate)

Polyesters, aromatic

- Poly(butylene terephthalate)
- Poly(ethylene-2,6-naphthalate)
- Poly(ethylene terephthalate)

Polyesters, unsaturated

Poly(ether ether ketone)

Poly(ether imide)

Poly(ether ketone)

Polyethers

- Poly(2,6-dimethyl-1,4-phenylene oxide)
- Poly(epichlorohydrin)
- Poly(ethylene oxide)
- Poly(methylene oxide)
- Poly(*p*-phenylene oxide)

- Poly(propylene oxide)
- Poly(tetrahydrofuran)
- Poly(trimethylene oxide)

Poly(ether sulfones)

- Bisphenol-A polysulfone
- Poly(ether sulfone)

Poly(ethyl acrylate)

Polyethylene, elastomeric (very highly branched)

Poly(ethylene imine)

Polyethylene, linear high-density

Polyethylene, linear low-density

Polyethylene, low-density

Polyethylene, metallocene linear low-density

Poly(ethylene-2,6-naphthalate)

Poly(ethylene oxide)

Poly(ethylene sulfide)

Poly(ethylene terephthalate)

Poly(ferrocenyldimethylsilane)

Polyflon

Polyformal

Polygermanes

Polygermylenes

Polyglycine

Poly(glycolic acid)

Polyheterocyclics

Polypyrrole

Polyquinoline

Polythiophene

Poly(hexamethylcyclodisilazane)

Poly(hexamethylene adipamide)

Poly(hexamethylene decanoamide)

Poly(hexamethylene sebacamide)

Poly(hexene-1)

Poly(*n*-hexyl isocyanate)

Poly(hydridosilsesquioxane)

Polyhydrosilsesquoxane

Poly(4-hydroxy benzoic acid)

Poly(hydroxybutyrate)

Poly(3-hydroxybutyrate)

Poly(alpha-hydroxy esters)

Poly(glycolic acid)

Poly(lactic acid)

Poly(2-hydroxyethyl methacrylate)

Polyimides

Poly(amide imide)

Poly(bis maleimide)

Poly(ether imide)

Poly(pyromellitimide-1,4-diphenyl ether)

Poly(iminoadipolyiminohexamethylene)

Poly[imino(1,6-dioxohexamethylene) iminohexamethylene]

Poly(iminoethylene)

Poly(iminohexamethylene-iminosebacoyl)

Poly[imino-1,6-hexanediylimino(1,10-dioxo-1,10-decanediyl)]

Poly[imino-1,6-hexanediylimino(1,12-dioxo-1,12-dedecanediyl)]

Poly(imino-1,4-phenyleneiminocarbonyl-1,4-phenylenecarbonyl)

Poly(isobutylene), butyl rubber, halobutyl rubber

Poly(isocyanates)

Poly(*n*-butyl isocyanate)

Poly(*n*-hexyl isocyanate)

Poly(isocyanide)

Poly(isonitrile)

cis-1,4-Polyisoprene

trans-1,4-Polyisoprene

Poly(N-isopropyl acrylamide)

Polyketones

- Poly(ether ether ketone)
- Poly(ether ketone)

Poly(lactic acid)

Polylaurolactam

Polylite

Polymeric selenium

Polymeric sulfur

Poly(methacrylic acid)

Poly(methyl acrylate)

Poly(methylacrylonitrile)

cis-1,4-Poly(2-methylbutadiene)

Poly(N-methylcyclodisilazane)

Poly(methylene oxide)

Poly(methyl methacrylate)

Polymethylpentene

Poly(4-methyl pentene-1)

Polymethylphenylsilane

Poly(methylphenylsiloxane)

Poly(methylphenylsilylene)

Poly(methylsilmethylene)

Poly(methylsilsesquioxane)

Poly(alpha-methylstyrene)

Poly(*p*-methylstyrene)

Poly(methyltrifluoropropylsiloxane)

Polymide 11

Polynitrile

Poly(norbornene)

Polyoctenamer

Poly(1-octenylene)

Polyolefin copolymers

- Ethylene-propylene-diene monomer elastomers
- Polyethylene, linear low-density

Poly(alpha-olefin copolymer)

Polyolefin elastomer

Polyolefin plastomers

Poly(alpha-olefins)

- Poly(butene-1)
- Polyethylene, elastomeric (very highly branched)
- Polyethylene, linear high-density
- Polyethylene, linear low-density
- Polyethylene, low-density
- Polyethylene, metallocene linear low-density

- Poly(hexene-1)
- Poly(4-methyl pentene-1)
- Polypropylene, atactic
- Polypropylene, elastomeric (stereoblock)
- Polypropylene, isotactic
- Polypropylene, syndiotactic
- Poly(tetrafluoroethylene)

Poly[oxy(dimethylsilylene)]

Polyoxymethylene

Poly[oxy(methylphenylsilylene)]

Poly(oxy-1-oxo-3-methyl-trimethylene)

Polypentenamer

Poly(1-pentenylene)

Polypeptides and proteins

- Collagen
- Elastic, plastic, and hydrogel-forming protein-based polymers
- Gelatin
- Poly(L-alanine)
- Poly(gamma-benzyl-L-glutamate)
- Polyglycine
- Silk protein

Poly(1,4-phenylene)

Poly(*p*-phenylene)

Poly(*p*-phenylene-2,6-benzobisthiazolediyl)

Poly(*p*-phenylene-2,6-benzoxazolediyl)

Poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole]

Poly(*m*-phenylene isophthalamide)

Poly(*p*-phenylene oxide)

Poly(*p*-phenylene sulfide)

Poly(*p*-phenylene terephthalamide)

Poly(1,4-phenylene vinylene)

Poly(*p*-phenylene vinylene)

Poly(alpha-phenylethyl isocyanide)

Poly(phenylmethylsiloxanes), cyclic

Poly(phenylsiloxane), cyclolinear

Poly(phenylsilsesquioxane)

Poly(phenyl/tolylsiloxane)

Polyphosphates

Poly(phosphazene), bioerodible

Poly(phosphazene) elastomer

Poly(phosphazene), semicrystalline

Polyphosphazenes

    - Poly(aryloxy)thionylphosphazenes
    - Poly(phosphazene), bioerodible
    - Poly(phosphazene) elastomer
    - Poly(phosphazene), semicrystalline
- Poly(phosphonate)
- Polyphthalamide
    - Nylon 6 copolymer
    - Nylon 6,6 copolymer
- Polypropylene, atactic
- Polypropylene, elastomeric (stereoblock)
- Polypropylene, isotactic
- Poly(propylene oxide)
- Poly(propylene sulfide)
- Polypropylene, syndiotactic
- Polypropylenimine dendrimers
- Poly(pyromellitimide-1,4-diphenyl ether)
- Polypyrrole
- Polyquinoline
- Poly(rotaxane), example 1
- Poly(rotaxane), example 2
- Polysaccharides
    - Cellulose

Chitin

Glycogen

Polysar S

Polysar SS

Poly(silaethylene)

Polysilanes

Poly(di-*n*-hexylsilylene)

Poly(dimethylsilylene)

Poly(dimethylsilylene-*co*-phenylmethylsilylene)

Poly(methylphenylsilylene)

Polysilastyrene

Polysilazanes

Hydridopolysilazane

Poly(N-methylcyclodisilazane)

Polysiloxanes

Poly(di-*n*-butylsiloxane)

Poly(diethylsiloxane)

Poly(di-*n*-hexylsiloxane)

Poly(dimethylsiloxane)

Poly(dimethylsiloxanes), cyclic

Poly(di-*n*-pentylsiloxane)

Poly(diphenylsiloxane)

Poly(di-*n*-propylsiloxane)

Poly(hydridosilsesquioxane)

Poly(methylphenylsiloxane)

Poly(methylsilsesquioxane)

Poly(methyltrifluoropropylsiloxane)

Poly(phenylsilsesquioxane)

Poly(phenyl/tolylsiloxane)

Poly(silphenylene-siloxanes)

Poly(silphenylene-siloxanes)

Poly(silylenemethylene)

Polystyrene

Polystyrene, head-to-head

Polystyrene, syndiotactic

Polysulfides

Poly(ethylene sulfide)

Poly(*p*-phenylene sulfide)

Poly(propylene sulfide)

Polysulfone, bisphenol-A

Poly(sulfur nitride)

Poly(tetrafluoroethylene)

Poly(tetrahydrofuran)

Polythiazyl

Poly(thionylphosphazene)

Polythiophene

Poly[(2,2,2,-trifluoroethoxy)phosphazene]

Poly(1,3-trimethyleneimine) dendrimers

Poly(trimethylene oxide)

Poly[1-(trimethylsilyl)-1-propyne]

Polyurea

Polyurethane

Polyurethane elastomers

Polyurethane urea

Poly(vdf-hfp)

Poly(vinyl acetate)

Poly(vinyl alcohol)

Poly(vinyl butyral)

Poly(N-vinyl carbazole)

Poly(vinyl chloride)

Poly(vinyl chloride), head-to-head

Poly(vinylferrocene)

Poly(vinyl fluoride)

Poly(vinylidene chloride)

Poly(vinylidene fluoride)

Poly(vinylidene fluoride-co-hexafluoropropylene)

Poly(vinyl methyl ether)

Poly(vinylmethylsiloxanes), cyclic

Poly(4-vinyl pyridine)

Poly(N-vinyl pyrrolidone)

Poly(*p*-xylylene)

POP

POPAM dendrimers

Poval

Povidone

PP

PPA

PPBA

PPE

- Poly(2,6-dimethyl-1,4-phenylene oxide)
- Poly(p-phenylene oxide)

PPHOS

PPMS

PPMS, cyclic

PPO

Poly(2,6-dimethyl-1,4-phenylene oxide)

Poly(p-phenylene oxide)

Poly(propylene oxide)

PPO

PPP

PPS

Poly(p-phenylene sulfide)

Poly(phenylsilsesquioxane)

Poly(propylene sulfide)

PPSQ

PPTA

PP/TS

PPV

PPX

PPy

PQ

PR

Poly(rotaxane), example 1

Poly(rotaxane), example 2

2-Propenamide homopolymer

Protein-based polymers

Proteins and polypeptides

- Collagen
- Elastic, plastic, and hydrogel-forming protein-based polymers
- Gelatin
- Poly(L-alanine)
- Poly(gamma-benzyl-L-glutamate)
- Polyglycine
- Silk protein

PS

PSE

PSF

PSM

PSS

PT

PTFE

PTFP

PTHF

PTMO

PTMSP

PTP

PU

- Polyurea

Polyurethane

Polyurethane elastomers

Polyurethane urea

PUR

Polyurea

Polyurethane

Polyurethane elastomers

PUU

PV-116 resin

PVA

PVAC

PVB

PVC

PVDC

PVDF

PVF

PVF2

PVK

PVM

PVME

PVMS, cyclic

PVP

Poly(4-vinyl pyridine)

Poly(N-vinyl pyrrolidone)

P4VP

Rayon

Regenerated cellulose

Reillex

Reny

Resimene

Resoles

Rexflex

Rextac

Rhovinal B

Rigid linear aromatic polyester

Rigid-rod polymers

Poly(benzimidazole)

Poly(benzobisoxazole)

Poly(benzobisthiazole)

Rilsan A

Rilsan B

Rubber

- Polychloroprene
- Poly(isobutylene), butyl rubber, halobutyl rubber
- cis-1,4-Polyisoprene

Ryton

Saflex

SAN

Saran (copolymer)

Saturated thermoplastic elastomer

SB

SBR

SCC

Semicrystalline poly(phosphazene)

Semi-inorganic and inorganic polymers

- Poly[(n-butylamino)thionylphosphazene]
- Poly(dimethylferrocenylethylene)
- Poly(ferrocenyldimethylsilane)
- Polygermanes
- Polymeric selenium
- Polymeric sulfur
- Polyphosphates
- Poly(phosphonate)
- Poly(sulfur nitride)

Poly(vinylferrocene)

SiB

Silarylene-siloxane polymers

Silicon (germanium) oxo hemiporphyrazine polymers

Silk

Silk protein

Siloxane ladder polymers

Poly(hydridosilsesquioxane)

Poly(methylsilsesquioxane)

Poly(phenylsilsesquioxane)

Silphenylenes

Single site catalyzed LLDPE

Skyprene

S'Lec

SMMA

$(SN)_x$

Sokalan

Solef

Solprene

Soltex

Spectratech

Spidroin

s-PP

sPP

SPS

Srereon

SSC LLDPE

Stanyl

Starburst dendrons and dendrimers

Starch

Styrene-acrylonitrile

Styrene-butadiene elastomers

Styrene-methylmethacrylate copolymer

Styrofoam

Sulfo-EPDM ionomers

Sulfo-ethylene-propylene-diene monomer ionomers

SupersoftPP

Surlyn

Syndiotactic polypropylene

Syndiotactic polystyrene

Synpol

Technyl D

Tecnoflon

Tedlar PVF film

Tedlar SP film

Teflon

Teijinconex

Telene (copolymer)

ter-Polymer elastomer

Thermoplastics

- Epoxy resins
- Kraton D1100 SBS
- Kraton G1600 SEBS
- Poly(amide imide)
- Poly(butylene terephthalate)
- Poly(epsilon-caprolactone)
- Poly(2,6-dimethyl-1,4-phenylene oxide)
- Poly(ether imide)
- Poly(ethylene-2,6-naphthalate)
- Poly(ethylene terephthalate)
- Poly(methylene oxide)
- Poly(*p*-phenylene oxide)

Thermoplastic saturated elastomer

Thermoplastic unsaturated elastomer

Thermoset polymers

- Alkyd resins
- Amino resins
- Epoxy resins
- Phenolic resins
- Poly(bis maleimide)
- Polyesters, unsaturated

Thermoset resin

Tohprene

TOR

Torelina

Torlon

TP 301

TPX

Trosofioil

TW241F10

TW300

Tylac

Tyril

UBE Nylon 12

Udel P1700

Udel P3500

Ultem

Ultraform

Ultra-low-density ethylene copolymer

Ultramid

Ultramid A

Ultramid S

Ultramid T

Ultrathene

Unsaturated polyesters

Unsaturated polymers

- Polyacetylene
- Polyaniline
- Poly[1-(trimethylsilyl)-1-propyne]

Unsaturated thermoplastic elastomer

Urea resins

Vespel

Vestamid

Vestenamer

Vestolite

Victrex

Victrex 100P

Victrex 200P

Vinoflex

Vinol

Vinylidene fluoride–hexafluoropropylene elastomers

Vinylidene polymers

- Poly(chlorotrifluoroethylene)
- Poly(cyclohexyl methacrylate)
- Poly(2-hydroxyethyl methacrylate)
- Poly(isobutylene), butyl rubber, halobutyl rubber
- Poly(methacrylic acid)
- Poly(methyl methacrylate)
- Poly(vinylidene chloride)
- Poly(vinylidene fluoride)

Vinylite XYHL

Vinyl polymers

- Polyacrylamide
- Poly(acrylic acid)
- Poly(*p*-chlorostyrene)
- Poly(ethyl acrylate)
- Poly(N-isopropyl acrylamide)
- Poly(methyl acrylate)

- Poly(alpha-methylstyrene)
- Poly(*p*-methylstyrene)
- Polystyrene
- Polystyrene, syndiotactic
- Poly(vinyl acetate)
- Poly(vinyl alcohol)
- Poly(vinyl butyral)
- Poly(N-vinyl carbazole)
- Poly(vinyl chloride)
- Poly(vinyl fluoride)
- Poly(vinyl methyl ether)
- Poly(4-vinyl pyridine)
- Poly(N-vinyl pyrrolidone)

Vistalon derivative

Viton

Wacker SWS101 fluid

Xarec

Zytel

TECHNICAL SUPPORT

If you require assistance in using this online application, please send e-mail to: polymer@oup-usa.org.

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Acrylonitrile-butadiene elastomers

SHUHONG WANG

ACRONYM, TRADE NAMES NBR, Chemigum® (The Goodyear Tire & Rubber Co.), Hycar® (BF Goodrich Specialty Chemicals), JSR (Japan Synthetic Rubber Co.), Krynac® (Bayer AG), NIPOL (Nippon Zeon Co.), Nysyn® (DSM Copolymer Rubber and Chemical Co.), Paracril® (Uniroyal Chemical Co.)

CLASS Chemical copolymers

STRUCTURE $-[CH_2-CH{=}CH-CH_2]_m-[CH_2-\underset{\underset{\displaystyle C{\equiv}N}{|}}{CH}]_n-$

MAJOR APPLICATIONS Hoses where oil, fuel, chemicals, and solutions are transported. Oil-drilling industry. Powder and particulate forms in cements and adhesives. Modification of PVC and ABS to improve impact resistance.

PROPERTIES OF SPECIAL INTEREST Special-purpose, oil-resistant rubbers. Balance of low-temperature, oil, fuel, and solvent resistance. Good abrasion resistance, gas permeability, and thermal stability. Good strength.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	26–27% ACN	0.92	(1)
Glass transition temperature T_g	K	~20% ACN	213	(2)
		~30% ACN	231	
		~34% ACN	238	
		~40% ACN	255	
		~48% ACN	263	
Service temperature (max)	K	9% N	373	(3)
Solubility parameter	$(MPa)^{1/2}$	25% ACN, 25°C, calc.	18.93	(4)
Theta temperature θ	K	26% ACN, cyclohexane/MEK (64/36)	293.2	(5)
		40% ACN, cyclohexane/MEK (52.5/47.5)	295.2	

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Acrylonitrile-butadiene elastomers

Volume swell (%) (Black loaded vulcanizate, 72 h at room temperature, or 100°C with *)[2]

Solvent	17% ACN	34% ACN	37% ACN
Lard*	18	−2	−3
Butter fat*	29	−3	−3
Lanolin*	20	0	−1.5
Margarine*	24	−5	−5
Stearic acid*	26	23	−2
Oleic acid	20	3	0
Cod liver oil	5	0	0
Dehydrogenated corn oil	3	0	0
Automobile lube oil (SAE−20)	0	0	0
Automobile hydraulic fluid	8	8	6
Jet aircraft fuel			
18% aromatic, 28% olefin	60	14	11
21% aromatic, 0.1% olefin	38	9	5
Ethylene glycol	0	0	0
Automobile gasoline	39	8	6
Skydrol hydraulic fluid	112	59	41
Dioctyl phthalate	52	6	2
Dibutyl phthalate	119	76	52
Tricresyl phosphate	50	21	16
Butyl carbitol formal (polyether)	92	32	21
Bis(dimethyl benzyl)ether	147	45	29
Liquid polyester	−2	0	−3
Triglycol dioctylate	83	12	5
Tributoxy ethyl phosphate	67	29	17

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength	MPa	Unfilled, vulcanizate (26 ∼ 27% ACN)	4 ∼ 7	(1)
Ultimate elongation	%	–	350 ∼ 800	(1)

PROPERTY	UNITS	VALUES							REFERENCE
	ACN %	40	33	33	33	33	27	20	
	Polymer Mooney	60	30	50	70	85	50	40	
Tensile strength	MPa	17.9	15.8	16.0	17.6	19.5	14.2	13.4	(6)
Ultimate elongation	%	466	478	433	357	439	334	387	(6)
Modulus, 100%	MPa	3.6	3.1	3.2	3.9	3.5	3.7	2.9	(6)
Modulus, 200%	MPa	8.6	7.0	7.7	9.5	8.9	8.5	7.0	(6)
Modulus, 300%	MPa	13.0	10.5	11.7	14.8	14.1	12.8	10.5	(6)
Hardness	Shore A values	68	67	66	67	66	67	64	(6)

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PROPERTY	UNITS	VALUES							REFERENCE
	ACN %	40	33	33	33	33	27	20	
	Polymer Mooney	60	30	50	70	85	50	40	
		Oven aging at 100°C, 70 h							
Tensile change	%	3	5	5	1	−9	8	−1	(6)
Elongation change	%	−12	−17	−15	−10	−25	−10	−21	(6)
Hardness change	%	4	4	4	4	4	4	3	(6)
		Oven aging at 121°C, 70 h							
Tensile change	%	3	9	6	8	1	16	4	(6)
Elongation change	%	−24	−21	−21	−8	−21	−10	−24	(6)
Hardness change	%	6	6	6	5	5	5	5	(6)
		Fluid aging at 121°C in ASTM oil No. 1							
Tensile change	%	6	12	15	9	8	6	13	(6)
Elongation change	%	−24	−26	−11	−13	−18	−18	−17	(6)
Hardness change	%	9	9	9	7	8	5	−2	(6)
Volume swell	%	−6.5	−5.9	−5.2	−5.2	−4.6	−2.6	0.9	(6)
		Fluid aging at 121°C in ASTM oil No. 3							
Tensile change	%	1	11	8	8	−1	0	−27	(6)
Elongation change	%	−20	−11	−4	1	−16	−11	−35	(6)
Hardness change	%	3	0	0	0	1	−6	−9	(6)
Volume swell	%	1.8	5.6	7.8	8.2	6.6	18	35	(6)
		Fluid aging at 23°C in ASTM Fuel B							
Tensile change	%	−43	−43	−42	−43	−46	−43	−54	(6)
Elongation change	%	−42	−40	−40	−41	−45	−44	−59	(6)
Hardness change	%	−9	−12	−10	−9	−9	−13	−14	(6)
Volume swell	%	18	26	28	28	28	38	53	(6)
		Fluid aging at 23°C in ASTM Fuel C							
Tensile change	%	−54	−51	−57	−55	−58	−58	−66	(6)
Elongation change	%	−58	−52	−58	−54	−59	−61	−72	(6)
Hardness change	%	−11	−15	−12	−10	−10	−13	−13	(6)
Volume swell	%	37	45	50	48	46	68	94	(6)
		Fluid aging at 100°C in distilled water							
Tensile change	%	−5	−8	−2	8	−8	−3	5	(6)
Elongation change	%	−18	−26	−18	−1	−23	−16	−8	(6)
Hardness change	%	0	−1	0	0	0	0	0	(6)
Volume swell	%	3.6	3.6	4.4	3.2	3.9	2.4	2.1	(6)

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PROPERTY	UNITS	VALUES							REFERENCE
	ACN %	40	33	33	33	33	27	20	
	Polymer Mooney	60	30	50	70	85	50	40	
Compression set	%	100°C, 70 h (ASTM D395, method B)							
		10.1	12.5	10.8	8.4	13.2	10.1	11.2	(6)
		121°C, 70 h (ASTM D395, method B)							
		24.0	26.0	23.0	20.1	23.9	24.0	25.3	(6)
Rebound	%	Goodyear–Healey method, 23°C							
		42	57	58	59	57	61	64	(6)
		Goodyear–Healey method, 100°C							
		60	74	76	77	76	78	79	(6)
Brittle temperature	K	245.5	236.5	234.7	234.1	234.1	222.1	218.5	(6)
Gehman temperature		Torsion							
T(2)	K	269	258	257	256	257	252	246	(6)
T(5)	K	262	253	251	251	252	248	241	(6)
T(10)	K	259	251	249	249	250	245	239	(6)
T(100)	K	255	245	242	244	244	240	232	(6)
Low temperature retraction, TR–10	K	50% elongation							
		252	246	244	244	246	241	231	(6)

* NBR compound formulation—Polymer: 100 phr, N774: 60 phr, ZnO: 4 phr, Wingstay 100: 2 phr, Paraplex G–25: 5 phr, TP 95 Plasticizer: 7 phr, METHYL TUADS: 2 phr, AMAX: 2 phr, Stearic Acid: 0.5 phr, Sulfur: 0.4 phr.

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Alkyd resins

MEE Y. SHELLEY

TRADE NAMES Plaskon, Durez, Glaskyd

CLASS Thermoset polymers (polyesters modified with monobasic fatty acids)

PRINCIPAL COMPONENTS Fatty acids and oils (e.g., lauric, palmitic, stearic, oleic, linoleic, linolenic, eleostearic, and licanic acids). Polyhydric alcohols (e.g., glycerol, pentaerythritol, ethylene glycol). Polybasic acids (e.g., phthalic acid/anhydride, maleic acid/anhydride, fumaric acid/anhydride).

MAJOR APPLICATIONS Paints, brushing enamels, and clear varnish. Industrial coatings (spraying, dipping, flow coating, roller coating). Industrial baking finishes.

PROPERTIES OF SPECIAL INTEREST Rapid drying. Good adhesion. Flexibility. Mar resistance and durability. Ester groups can be hydrolyzed under alkaline conditions.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Processing temperature	K	Molding, mineral filled (granular and putty)		(1)
		Compression	405–450	
		Injection	410–470	
		Transfer	430–460	
		Molding, glass fiber-reinforced		(1)
		Compression	420–450	
		Injection	410–470	
		Unspecified	425–440	(2)
Molding pressure	MPa	Molding, mineral filled (granular and putty)	14–140	(1)
		Molding, glass fiber-reinforced	14–170	
Compression ratio		Molding, mineral filled (granular and putty)	1.8–2.5	(1)
		Molding, glass fiber-reinforced	1–11	
Linear mold shrinkage	ratio	Molding, mineral filled (granular and putty)	0.003–0.010	(1)
		Molding, glass fiber-reinforced	0.001–0.010	(1)
		Unspecified	0.002–0.007	(2)
Density	$g\,cm^{-3}$	Molding, mineral filled (granular and putty)	1.6–2.3	(1)
		Molding, glass fiber-reinforced	2.0–2.3	(1, 3)
		Unspecified	2.05–2.16	(2)
		Coating	1.2	(3)
Water absorption	%	Molding, mineral filled (granular and putty), 1/8 in. thick specimen, 24 h	0.05–0.5	(1)
		Molding, glass fiber-reinforced, 1/8 in. thick specimen, 24 h	0.03–0.5	(1)
		Coating	2	(3)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength at break	MPa	Molding, mineral filled (granular and putty)	20–60	(1)
		Molding, glass fiber-reinforced	30–66	(1)
		Molding, glass fiber-filled	41	(3)
		Unspecified	40–60	(2)
		Coating	35	(3)
Elongation	%	Coating	65	(3)
		Molding, glass fiber-filled	2	

Solubility parameters[4,5]

Conditions	Hansen parameters (MPa)$^{1/2}$			
	δ_d	δ_p	δ_h	δ_t
Long oil (66% oil length, Plexal P65, Polyplex)	20.42	3.44	4.56	21.20
Short oil (coconut oil 34% phthalic anhydride; Plexal C34)	18.50	9.21	4.91	21.24

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile yield strength	MPa	Unspecified	45–48	(2)
Compressive strength (rupture or yield)	MPa	Molding, mineral filled (granular and putty)	83–260	(1)
		Molding, glass fiber-reinforced	100–250	(1)
		Unspecified	150–190	(2)
Flexural strength (rupture or yield)	MPa	Molding, mineral filled (granular and putty)	40–120	(1)
		Molding, glass fiber-reinforced	60–180	(1)
		Unspecified	60–160	(2)
		Molding, glass fiber-filled	103	(3)
Tensile modulus	MPa	Molding, mineral filled (granular and putty)	3,000–20,000	(1)
		Molding, glass fiber-reinforced	14,000–19,000	
Compressive modulus	MPa	Molding, mineral filled (granular and putty)	14,000–20,000	(1)
		Molding, glass fiber-filled	140	(3)
Flexural modulus	MPa	Molding, mineral filled (granular and putty), 296 K	14,000	(1)
		Molding, glass fiber-reinforced, 296 K	14,000	(1)
		Unspecified	14,000–20,000	(2)
Impact strength, Izod	J m^{-1}	Molding, mineral filled (granular and putty)	16–27	(1)
		Molding, glass fiber-reinforced	27–850	(1)
		Unspecified	17–400	(2)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Hardness	Rockwell	Molding, mineral filled (granular and putty)	E98	(1)
	Rockwell	Molding, glass fiber-reinforced	E95	(1)
	Rockwell	Molding, glass fiber-filled	E80	(3)
	Shore	Coating	D80	(3)
Deflection temperature	K	Molding, mineral filled (granular and putty) under flexural load, 1.82 MPa	450–530	(1)
		Molding, glass fiber-reinforced under flexural load, 1.82 MPa	480–530	(1)
		Molding, glass fiber-filled, 1.82 MPa	470	(3)
Maximum resistance to continuous heat	K	Coating	360	(3)
		Molding, glass fiber-filled	470	
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	Granular and putty, mineral filled	0.5–1.0	(1)
		Glass fiber-reinforced	0.6–1.0	
Dielectric strength	$V\,mil^{-1}$	Molding, mineral filled (granular and putty)	350–450	(1)
		Molding, glass fiber-reinforced	259–530	(1)
		Glass-filled	375	(6)
		Mineral-filled	400	(6)
Volume resistivity	ohm cm	Glass-filled	10^{15}	(6)
		Mineral-filled	10^{14}	
Dielectric constant	–	Glass-filled, 1 MHz	4.6	(6)
		Mineral-filled, 1 MHz	4.7	(6)
		Unspecified, 1 MHz	4.7–6.7	(2)
		Coating	4	(3)
Dissipation factor at 1 MHz	–	Glass-filled	0.02	(6)
		Mineral-filled	0.02	(6)
		Unspecified	0.009–0.02	(2)

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Amino resins

MILIND SOHONI

ALTERNATIVE NAMES Melamines, urea resins

TRADE NAMES Resimene (Solutia, Inc.), Cymel (Cytek Industries, Inc.)

CLASS Thermoset polymers; chemical copolymers

TYPICAL COMONOMERS Melamines, urea, formaldehyde, ethylene urea, benzoguanamine, thiourea, acetoguanamine

POLYMERIZATIONS Condensation

MAJOR APPLICATIONS Molding resins, adhesives, coatings, treatment of paper and textiles, automobile tires

PROPERTIES OF SPECIAL INTEREST Hardness, nonflammability, arc resisitance, thermal properties, lightfastness

Properties of amino-formaldheyde molding compounds[(1)]

Property	Units	Resin and filler	
		Urea-formaldehyde, alpha-cellulose	Melamine-formaldehyde, alpha-cellulose
Pigmentation and coloring possibilities	–	Unlimited	Unlimited
Appearance	–	Translucent to opaque	Translucent to opaque
Molding qualities	–	Excellent	Excellent
Type of resin	–	Thermosetting	Thermosetting
Molding temperature	°F (°C)	275–300 (135–177)	280–370 (138–188)
Molding pressure	psi	2,000–8,000	1,500–8,000
Mold shrinkage	in in^{-1}	0.006–0.014	0.005–0.015
Specific gravity	–	1.47–1.52	1.47–1.52
Tensile strength	psi	6–13 $\times 10^3$	7–13 $\times 10^3$
Flexural strength	psi	10–16 $\times 10^3$	10–16 $\times 10^3$
Notched Izod impact strength	ft-lb in^{-1}	0.25–0.4	0.24–0.35
Rockwell hardness	–	M 110–M 120	M 110–M 125
Thermal expansion	°C^{-1}	2.2–3.6 $\times 10^{-6}$	4.0 $\times 10^{-6}$
Deflection temperature under load	°F	260–290	410
Dielectric strength, short time, 0.125 in thickness	V mil^{-1}	300–400	300–400
Dielectric constant	–	6–8	7.2–8.4
Dissipation factor	–	0.025–0.035	0.027–0.045
Arc resistance	s	80–150	110–180
Cold-water absorption, room temp.			
24 h, 0.125 in thickness	%	0.4–0.8	0.1–0.6
7 days	mg (100 cm^2)$^{-1}$	800	270
Boiling water test, 10 min, 100°C	%	3.4	0.4
Burning rate	–	Self-extinguishing	Self-extinguishing
Effect of sunlight	–	Pastels turn gray	Slight color change

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Curing range of urea- and melamine-formaldehyde molding compounds[(1)]

Cure time (min)	Cure temperature (°C)							
	0.5	1	1.5	2	3	4	6	8
Urea-formaldehyde base								
Upper limit	–	170	167	163	158	154	148	145
Optimum temperature	–	169	164	160	155	151	145	140
Lower limit	–	167	160	156	150	145	139	135*
Melamine-formaldehyde								
Upper limit	187	182	179	177	172	169	165	161
Optimum temperature	175	167	159	154	146	140	130*	120*
Lower limit	172	155	145	138	125*	120*	115*	110*

*Value extrapolated.

Rate constants for urea-formaldehyde reactions at 35°C and pH 4.0[(3)]

Reaction*	Rate constant K, L $(\mathrm{s\,mol})^{-1}$
$U + F \rightarrow UF$	4.4×10^{-4}
$UF + U \rightarrow U{-}CH_2{-}U$	3.3×10^{-4}
$UF + UF \rightarrow U{-}CH_2{-}UF$	0.85×10^{-4}
$UF_2 + UF \rightarrow FU{-}CH_2{-}UF$	0.5×10^{-4}
$UF_2 + UF_2 \rightarrow FU{-}CH_2{-}UF_2$	$<3 \times 10^{-6}$

*U = urea. F = formaldehyde.

^{1}H NMR chemical shifts† for melamine resins[(2)]

Proton	Chemical shift	Structure
$-NH_2^*$	5.8–6.2	Broad singlet
$-NH^*$	7.2–7.4	Broad singlet
$-N{-}CH_2OH^*$	5.4–5.6	Broad triplet
$-N{-}CH_2^*OH$	–	–
$-N{-}CH_2^*OR$	4.6–5.1	Broad peak
$-N{-}CH_2^*{-}N{-}$	–	–
$-O{-}CH_3^*$	3.2	Singlet
$-O{-}CH_2^*CH_3$	3.0–3.2	Quadruplet
$-O{-}CH_2CH_3^*$	1.2	Triplet
$-O{-}CH_2^*CH_2CH_3$	3.5	Triplet
$-O{-}CH_2CH_2^*CH_3$	1.5	Multiplet
$-O{-}CH_2CH_2CH_3^*$	1.1	Triplet
$-O{-}CH^*(CH_3)_2$	3.8–4.0	Multiplet
$-O{-}CH(CH_3^*)_2$	1.0–1.1	Doublet
$-O{-}CH_2^*CH_2CH_2CH_3$	3.0–3.3	Triplet
$-O{-}CH_2CH_2^*CH_2^*CH_3$	1.0–1.5	Multiplet
$-O{-}CH_2CH_2CH_2CH_3^*$	0.7–1.0	Triplet
$-O{-}CH_2^*CH(CH_3)_2$	3.5	Multiplet
$-O{-}CH_2CH^*(CH_3)_2$	1.5	Multiplet
$-O{-}CH_2CH(CH_3^*)_2$	0.8	Doublet

†Chemical shifts in ppm relative to TMS.

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^{13}C NMR chemical shifts† for melamine resins[5]

Carbon atom	Chemical shift
N C^*-NH_2 N	167.4
N $C^*-NH(CH_2O-)$ N	166.0–166.6
N $C^*-N(CH_2O-)_2$ N	165.4–165.8
$-NHCH_2OC^*H_2O-$	93.0
$-N(C^*H_2OCH_3)_2$	76.8
$-NHC^*H_2OCH_3$	72.6
$-N(C^*H_2OC_4H_9)_2$	74.4
$-NHC^*H_2OC_4H_9$	71.0
$-NHC^*H_2OC^*H_2NH-$	68.0–69.0
$-NHC^*H_2OH$	64.5
$-N(CH_2OC^*H_3)_2$	55.4
$-NHCH_2OC^*H_3$	54.5
$-NCH_2OC^*H_2CH_2CH_2CH_3$	66.9
$-NCH_2OCH_2^*CH_2CH_2CH_3$	31.4
$-NCH_2OCH_2CH_2C^*H_2CH_3$	18.9
$-NCH_2OCH_2CH_2CH_2C^*H_3$	13.7
$-NCH_2OCH_2C^*H(CH_3)_2$	28.1
$-NCH_2OCH_2CH(C^*H_3)_2$	18.9

†Chemical shifts in ppm relative to TMS.

Melamine/formaldehyde reactions[2]

1. $-NCH_2OCH_3 + ROH \rightarrow -NCH_2OR + CH_3OH$
2. $2\,-NCH_2OCH_3 + H_2O \rightarrow -NCH_2N- + H_2C=O + 2CH_3OH$
3. $-NCH_2OCH_3 + -NH \rightarrow -NCH_2N- + CH_3OH$
4. $2\,-NCH_2OCH_3 \rightarrow -NCH_2N- + CH_3OCH_2OCH_3$
5. $-NCH_2OCH_3 + -NCH_2OH \rightarrow -NCH_2OCH_2N- + CH_3OH$
6. $-NCH_2OCH_3 + H_2O \rightarrow -NCH_2OH + CH_3OH$
7. $-NCH_2OH \rightarrow -NH + H_2C=O$
8. $-NCH_2OH + -NH \rightarrow -NCH_2N- + H_2O$
9. $2\,-NCH_2OH \rightarrow -NCH_2N- + H_2C=O + H_2O$
10. $-NCH_2OH + ROH \rightarrow -NCH_2OR + H_2O$
11. $2\,-NCH_2OH \rightarrow -NCH_2OCH_2N- + H_2O$

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Reaction constants for urea-formaldehyde at 35°C and pH 7.0[4]

Reaction	Second order reaction velocity constant, k_1 ($l\,mol^{-1}\,s^{-1}$)	Equilibrium constant, $K(k_2 k_1^{-1})$ ($mol\,l^{-1}$)
1. $U + F \underset{R_2}{\overset{R_1}{\rightleftharpoons}} UF$	0.9×10^{-4}	0.036
2. $UF + F \underset{R_2}{\overset{R_1}{\rightleftharpoons}} UF_2$	0.38×10^{-4}	0.22
3. $UF_2 + F \underset{R_2}{\overset{R_1}{\rightleftharpoons}} UF_3$	0.1×10^{-4}	1.2

Properties of melamine-formaldehyde laminates[1]

Property	Units	Melamine-formaldehyde laminate	
		Cellulose paper base	Glass fabric base
Coloring possibilities	–	Unlimited	Unlimited
Appearance	–	Translucent/opaque	Translucent/opaque
Laminating temperature	°F	270–320	270–300
Laminating pressure	psi	500–1,800	1,000–1,800
Specific gravity		1.4–1.5	1.82–1.98
Tensile strength	psi	$10–25 \times 10^3$	$25–40 \times 10^3$
Flexural strength	psi	$14–20 \times 10^3$	$40–65 \times 10^3$
Notched Izod impact strength	ft-lb in^{-1}	0.3–1.5	5–15
Rockwell hardness	–	M 110–M 125	M 115–M 125
Water absorption, 24 h, room temp., 0.125 in thickness	%	1.0–2.0	1.0–2.5
Effect of sunlight	–	Slight color change	Slight color change
Machining qualities	–	Fair	Fair
Thermal expansion	$°C^{-1}$	$0.7–2.5 \times 10^{-5}$ *	$0.7–1.2 \times 10^{-5}$
Resistance to heat (continuous)	°F	210–260	300
Burning rate	–	~ Nil	Nil
Dielectric strength, short time	V mil^{-1}	400–700	200–500
Dielectric constant, at 10^6 cps	–	6.4–8.5	6.0–9.0
Dissipation factor, at 10^6 cps	–	0.035–0.05	0.011–0.025
Arc resistance	s	100	175–200

*Cotton fabric filler.

Rate constants for melamine-formaldehyde resins at pH 7.7[6]

Reaction	Temp. (°C)	Second order rate constant of forward reaction, k_1	First order rate constant of reverse reaction, k_2
1. $M + F \rightleftharpoons MF$	50	1.4×10^{-3}	0.3×10^{-4}
	70	6.1×10^{-3}	3.5×10^{-4}
2. $MF + F \rightleftharpoons MF_2$	50	1.0×10^{-3}	1.4×10^{-4}
	70	5.4×10^{-3}	6.6×10^{-4}
3. $MF_2 + F \rightleftharpoons MF_3$	50	1.8×10^{-3}	–
	70	7.4×10^{-3}	–

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Typical properties of filled amino resin molding compounds[3]

Property	Units	Urea	Melamine			
		Alpha-cellulose	Alpha-cellulose	Macerated fabric	Asbestos	Glass fiber
Physical						
Specific gravity	–	1.47–1.52	1.47–1.52	1.5	1.7–2.0	1.8–2.0
Water absorption, 24 h, 3.2 mm thick	%	0.48	0.1–0.6	0.3–0.6	0.08–0.14	0.09–0.21
Mechanical						
Tensile strength	MPa (10^3 psi)	38–48 (5.5–7)	48–90 (7–13)	55–69 (8–10)	38–45 (5.5–6.5)	35–70 (5–10)
Elongation	%	0.5–1.0	0.6–0.9	0.6–0.8	0.3–0.45	
Tensile modulus	GPa (10^5 psi)	9–9.7 (13–14)	9.3 (13.5)	9.7–11 (14–16)	13.5 (19.5)	16.5 (24)
Hardness, Rockwell M	–	110–120	120	120	110	115
Flexural strength	MPa (10^3 psi)	70–124 (11–18)	83–104 (12–15)	83–104 (12–15)	52–69 (7.4–10)	90–165 (13–24)
Flexural modulus	GPa (10^5 psi)	9.7–10.3 (14–15)	7.6 (11)	9.7 (14)	12.4 (18)	16.5 (24)
Notch Impact strength	$J\,m^{-1}$ (ft-lb in^{-1})	14–18 (0.27–0.34)	13–19 (0.24–0.35)	32–53 (0.6–1.0)	16-21 (0.3–0.4)	32-1000 (0.6–18)
Thermal						
Thermal conductivity	10^{-4} J-cm s^{-1} cm^{-2} $°C^{-1}$ *	42.3	29.3–42.3	44.3	54.4–71	48.1
Coefficient of thermal expansion	10^{-5} cm cm^{-1} $°C^{-1}$ *	2.2–3.6	2.0–5.7	2.5–2.8	2.0–4.5	1.5–1.7
Deflection temperature at 1.8 MPa (264 psi)	°C	130	182	154	129	204
Flammability class	–	VO†	VO†	–	–	VO
Continuous no-load service temperature	°C	77‡	99‡	121	149	149–204
Electrical						
Dielectric strength	V/0.00254 cm					
Short time, 3.2 mm thick		330–370	270–300	250–350	410–430	170–300
Step by step		220–250	240–270	200–300	280–320	170–240
Dielectric constant, 22.8°C	–					
60 Hz		7.7–7.9	8.4–9.4	7.6–12.6	6.4–10.2	9.7–11.1
10^3 Hz		–	7.8–9.2	7.1–7.8	9.0	–
Dissipation factor, 22.8°C	–					
60 Hz		0.034–0.043	0.030–0.083	0.07–0.34	0.07–0.17	0.14–0.23
10^3 Hz		–	0.015–0.036	0.03–0.05	0.07	–
Volume resistivity, 22.8°C, 50% rh	ohm cm	$0.5–5.0 \times 10^{11}$	$0.8–2.0 \times 10^{12}$	$1.0–3.0 \times 10^{11}$	1.2×10^{12}	$0.9–2.0 \times 10^{11}$
Arc resistance	s	80–100	125–136	122–128	20–180	180–186

*To convert J to cal divide by 4.184.
†Applies to specimens thicker than 1.6 mm.
‡Based on no color change.

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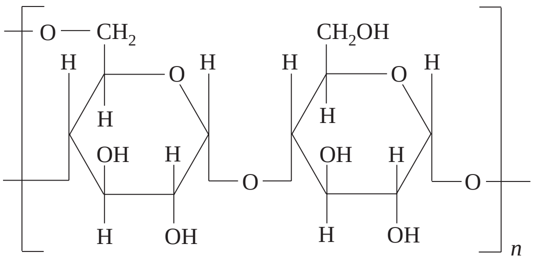
Amylopectin

W. BROOKE ZHAO

CLASS Carbohydrate polymers

STRUCTURE



MAJOR APPLICATIONS Thickeners, stabilizers, and adhesives.

PROPERTIES OF SPECIAL INTERESTS The highly branched nature of amylopectin accounts for the extreme brittleness of its films and extrudates. The extensive branching reduces chain entanglements usually required in high polymers to achieve satisfactory film properties.

PREPARATIVE TECHNIQUES Fractionation of starches. Native starches usually contain about 70–80% amylopectin. Genetic modification can result in starches having virtually no amylose content, such as waxy maize.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	Ranges	4.5×10^4–4.2×10^8	(1)
		Method: DMSO, light scattering		(2)
		Barley	4.0×10^7	
		Pea		
		Smooth	5.0×10^7	
		Wrinkled	5.0×10^7	
		Potato I	4.4×10^7	
		Potato II	6.5×10^6	
		Tapioca	4.5×10^7	
		Waxy maize	4.0×10^7	
		Waxy maize, sheared	1.0×10^6	
		Wheat	4.0×10^7	
Polydispersity index (M_w/M_n)	—	Range, depending on source	300–500	(1)
		In DMSO, GPC ($M_w = 15.96 \times 10^6$; $M_n = 8.5 \times 10^6$)	1.88	(3)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Degree of polymerization	–	Depending on plant source and methods of extraction	280–(1.45×10^6)	(1)
NMR	ppm	^{13}C chemical shift Solid state CP/MAS 25.18 MHz	 101.9–100.3 (C-1) 63.1 (C-6)	(4)
Surface tension	$mN\,m^{-1}$	–	35	(5)
Specific rotation [α]	Degrees	Solvent / λ (nm) Water / 135 1 M NaOH / 134 1 N KOH / – Ethylenediamine / – Ethylenediamine hydrate / – Formamide / –	 +200 +192 +163 +160 +173 +182 +167 +192	 (6) (7) (6) (7) (7) (7) (7) (7)
Refractive index increment dn/dc	$ml\,g^{-1}$	0.5 N KCl 1 N KOH Ethylenediamine Ethylenediamine hydrate Formamide Water	0.156 0.142 0.098 ± 0.001 0.092 ± 0.003 0.069 ± 0.002 0.151, 0.155	(8) (7) (7) (7) (7) (9)
Common solvents	Dimethyl sulfoxide, ethylene-diamine (hydrate and anhydrate), chloral hydrate, and hydrazine hydrate			(2)
Dilute-limit self diffusion coefficient	$m^2\,s^{-1}$	D_0 In DMSO In *d*-DMSO In H_2O Mass-weighted average molar mass ($D_0(M_w)$) In *d*-DMSO In D_2O Mass-*z* average molar mass ($D_0(M_z)$) In DMSO, 24°C	 8×10^{-13} $(3.2 \pm 0.7) \times 10^{-11}$ $(1.0 \pm 0.2) \times 10^{-11}$ $(9 \pm 2) \times 10^{-12}$ $(2.8 \pm 0.6) \times 10^{-12}$ $(13 \pm 3) \times 10^{-13}$ $(9 \pm 2) \times 10^{-13}$	 (10) (11) (11) (11) (11) (11) (12)
Diffusion coefficient	–	–	9×10^{-12}	(10)
$J = a/b$ (ratio of semi-axes of the particles)			38 28	(10) (3)

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Amylopectin

PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Sedimentation coefficient (s_0)	Svedberg	Plant source			(13)
		Rongotes		88 ± 3	
				115 ± 4	
				103 ± 1	
		Crossbow		65 ± 7	
				67 ± 1	
				73 ± 1	
		Aotea		105 ± 2	
		Karamu		87 ± 8	
		Hilgendorf		98 ± 4	
Hydrodynamic volume $(a^2/b)^{1/3}$	–	In DMSO		18(7)	(10)
Hydrodynamic radius (R_D)	nm	In DMSO		22(3)	(10)
		In *d*-DMSO		14	(11)
		In D_2O		82	(11)
Solvation coefficient (h)	$g\,g^{-1}$	Amylopectin/H_2O		0.25 ± 0.04	(11)
		Amylopectin/DMSO		0.6 ± 0.2	
Radius of gyration	Å	Solvent for light scattering	M_w		(7)
		1 N KOH	8.0×10^7	2050	
			1.0×10^8	2060, 2120	
		Ethylenediamine	7.5×10^7	2150, 2120	
		Ethylenediamine hydrate	9.5×10^8	2050, 2090	
		Formamide	1.66×10^8	2960, 2920	
		Water	4.3×10^7	1540, 1630	
Second virial coefficient A_2	$mol\,cm^3\,g^{-2}$	Solvent for light scattering	M_w		(7)
		1 N KOH	8.0×10^7	9.6×10^7	
			1.0×10^8	7.6×10^7	
		Ethylenediamine	7.5×10^7	2.4×10^7	
		Ethylenediamine hydrate	9.5×10^8	2.9×10^7	
		Formamide	1.66×10^8	8.0×10^7	
		Water	4.3×10^7	0	

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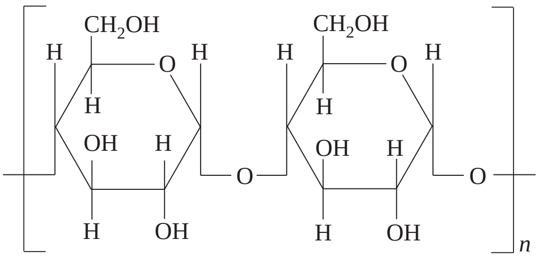
Amylose

W. BROOKE ZHAO

CLASS Carbohydrate polymers

STRUCTURE



MAJOR APPLICATIONS Adhesives, food, pharmaceutical, gels and foams, coating, and biodegradable packaging films.

PROPERTIES OF SPECIAL INTERESTS The linear glucan chains in amylose are responsible for its film-forming ability.

PREPARATIVE TECHNIQUES Fractionation of starches. Native starches contain about 20–30% amylose. Genetic modification can result in high amylose content (up to 80%).

PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Molecular weight	$g\,mol^{-1}$	Range		3.2×10^4–3.6×10^6	(1)
		Source	Methods		(2)
		Apple	Anaerobic, viscosity	2.4×10^5	
		Banana	Anaerobic, viscosity	2.7×10^5	
		Broad bean	Anaerobic, viscosity	2.9×10^5	
		Barley	Anaerobic, viscosity	3.0×10^5	
			DMSO, light scattering	2.11×10^6	
		Iris (rhizome)	Anaerobic, viscosity	2.9×10^5	
		Mango seed	Anaerobic, viscosity	2.9×10^5	
		Oat	Anaerobic, viscosity	2.1×10^5	
			DMSO, light scattering	2.19×10^6	
		Parsnip	Anaerobic, viscosity	7.1×10^5	
		Pea			
		Smooth	Anaerobic, viscosity	2.1×10^5	
		Wrinkled	Anaerobic, viscosity	1.6×10^5	
		Potato	Anaerobic, light scattering	4.9×10^5	
		Potato	DMSO, light scattering	1.9×10^6	
		Rubber seed	Anaerobic, light scattering	2.4×10^5	
		Rye	DMSO, light scattering	2.5×10^6	
		Sweet corn	Anaerobic, light scattering	1.8×10^5	
		Wheat	Anaerobic, light scattering	3.4×10^5	
		Wheat I	DMSO, light scattering	1.33×10^6	
		Wheat II	DMSO, light scattering	2.65×10^6	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Polydispersity index (M_w/M_n)	—	In DMSO, GPC, $M_w = 2.83 \times 10^5$, $M_n = 1.53 \times 10^5$	1.85	(3)
Degree of polymerization (DP)	—	Depending on plant source and extracting methods	200–22,000	(1)
Polymorphs	—	Alkali amylose after kept at 80% or higher relative humidity at 85–90°C	A-amylose	(2)
		Alkali amylose after kept at 80% or higher relative humidity at room temperature	B-amylose	
		V_h form after extensive drying	V_a-amylose	
		Crystallized from *n*-butanol	V_h-amylose	

Polymorphs	Lattice	Cell dimension (Å)			Cell angle	Helix symmetry	Interchain and intersheet spacings (Å)			Ref.
		a	*b*	*c*	γ		$d_{\uparrow\downarrow}$	d_{110}	*h*	
A	Orthorhombic	11.90	17.70	10.52	90	2 × 6/1 in 21.04 A repeat	10.66	9.87	3.51	(4)
B	Orthorhombic	18.50	18.50	10.40	90	2 × 6/1 in 20.8 A repeat	10.68	9.25	3.47	(4)
V_a	Orthorhombic	12.97	22.46	7.91	90	21 (~6/5)	12.97	11.23	1.32	(4)
V_h	Orthorhombic	13.7	23.7	8.05	90	6/5	13.69	11.86	1.34	(4)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Infrared absorption	cm^{-1}	OH stretching		(5)
		V-amylose (crystalline)	3,500–3,300 (broad)	
		B-amylose (crystalline)	3,500–3,300 (broad), 1,122	
		Amorphous	3,500–3,300 (sharper)	
		CH_2OH bending, V → B	1,263 → 1,254	
		CH_2 skeletal, V → B	946 → 936	
NMR	ppm	^1H chemical shift		
		DMSO-d_6 (100°C)	5.07 (H-1), 3.30 (H-2), 3.64 (H-3), 3.32 (H-4), 3.4 (H-5) 3.7 (H-6)	(6)
		D_2O, 500 MHz (75°C)	5.896 (d) (H-1), 4.162 (dd) (H-2), 4.478 (dd) (H-3), 4.162 (t) (H-4), 4.350 (H-5), 4.406 (dd) (H-6_a), 4.328 (dd) (H-6_b)	(7)
		^{13}C chemical shift	100.4 (C-1), 72.6 (C-2), 73.7 (C-3), 79.4 (C-4), 72.1 (C-5), 61.2 (C-6)	(6)
		Solid state CP/MAS		(8)
		A-amylose	102.30, 101.32, 100.05 (t) (C-1), 63.67, 62.73 (shoulder) (C-6)	
		B-amylose	101.71, 100.74 (d) (C-1) 62.69 (C-6)	
		V_h-amylose	103.85 (C-1), 62.21 (C-6)	
		V_a-amylose	103.76 (C-1), 61.79 (C-6)	

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Amylose

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Spin-spin coupling constant $^3J_{HH}$	Hz	D_2O, 500 MHz (75°C)	4.0 (H-1), 9.9 (H-2), 9.1 (H-3), 9.3 (H-4), 2.0 4.7 (H-5), 12 (H-6)		(7)
Dissociation constant pK_a	–	pH $= 11.2 \pm 0.1$	12.5 ± 0.2		(9)
		pH $= 12.5 \pm 1$	13.0 ± 0.1		
Degree of dissociation α	–	pH $= 11.2 \pm 0.1$	0.05		(9)
		pH $= 12.5 \pm 1$	0.26		
Electrophoretic mobility U	$cm^2\,V^{-1}\,s^{-1}$	pH $= 11.2 \pm 0.1$	3.5		(9)
		pH $= 12.5 \pm 1$	18.4		
Common solvents	Alkaline solutions, aqueous chloral hydrate, formamide, dichloroacetic acid, pyrrolidine, dimethyl sulfoxide, acetamide, ethylenediamine, piperazine, formic acid, and urea				(2)
Theta temperature Θ	K	0.33 M KCl	293–296		(10)
		DMSO/acetone 43.5%	298		(11)
Mark-Houwink parameters: K and a	–		$K \times 10^5$ (ml g^{-1})	a	(2)
		Water	13.2	0.68	
		0.5 N NaOH	1.44	0.93	
			3.64	0.85	
		0.15 N NaOH	8.36	0.77	
		0.2 N KOH	6.92	0.78	
		0.5 N KOH	8.5	0.76	
		1.0 N KOH	1.18	0.89	
		0.33 N KCl	113	0.50	
			112	0.50	
			115	0.50	
		0.5 N KCl	55	0.53	
			55	0.53	
		Aqueous KCl (acetate buffer)	59	0.53	
		Dimethyl sulfoxide	1.25	0.87	
			30.6	0.64	
			15.1	0.70	
			3.95	0.82	
		Ethylenediamine	15.5	0.70	
		Formamide	22.6	0.67	
			30.5	0.62	
Flexibility parameter	–	KCl · KOH, 25°C			(12)
		Hydrodynamic data in Θ condition	$\lambda_\theta = 2.70$		
		Stockmayer-Fixman plot	$\lambda_\theta = 2.58$		
		Extrapolation of λ tending to zero	$\lambda_{\theta,1/2} = 1.34$		
			$\lambda_{\theta,1/3} = 2.18$		
			$\lambda_{\theta,1/4} = 2.69$		

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Unperturbed chain dimension $\langle S\rangle^2/P$	$Å^2$	Solvent			(13)
		Me_2SO-H_2O		12.2	
		Five solvents		12.2	
		Me_2SO-KCl		12.2	
		Me_2SO-acetone		12.8	
		Me_2SO-acetone		13.2	
		Me_2SO-MeOH		14.6	
		H_2O-KCl		14.6	
		0.5 N NaOH		14.9	
		H_2O		14.7	
		Formamide		14.7	
		Me_2SO		14.7	
Second virial coefficient A_2	mol cm^3 g^{-2}	DP = 3,650, 20°C			
		DMSO/44% acetone		-2.3×10^{-6}	(14)
		DMSO/42% acetone		3.45×10^{-5}	(14)
		DMSO/39% acetone		1.322×10^{-4}	(14)
		Formamide		2.19×10^{-4}	(14)
		DMSO/30% acetone		2.59×10^{-4}	(14)
		DMSO/20% acetone		3.92×10^{-4}	(14)
		DMSO/10% acetone		4.78×10^{-4}	(14)
		DMSO		5.35×10^{-4}	(14)
		Ethylenediamine		5.64×10^{-4}	(14)
		0.5 N NaOH		4.88×10^{-4}	(14)
		Water		1.10×10^{-4}	(14)
		1 N KOH		8.9×10^{-5}	(11)
		0.5 KCl, 31°C		2.89×10^{-5}	(11)
		0.5 KCl, 28°C		1.41×10^{-5}	(11)
Expansion coefficient α	–	DP = 3,650, 20°C			(14)
		DMSO/44% acetone		0.96	
		MSO/42% acetone		1.1	
		DMSO/39% acetone		1.25	
		Formamide		1.47	
		DMSO/30% acetone		1.53	
		DMSO/20% acetone		1.73	
		DMSO/10% acetone		1.88	
		DMSO		2.0	
		Ethylenediamine		2.08	
		0.5 N NaOH		1.86	
		Water		1.59	
Radius of gyration	Å	Solvent for L.S.	M_w		(11)
		DMSO	2.22×10^6	935	
		1 N KOH	2.23×10^6	912	
		0.5 N KCl, 31°C	2.44×10^6	763	
		0.5 N KCl, 28°C	–	745	
		DMSO	1.35×10^6	724	
		DMSO	1.05×10^6	656	
		DMSO	8.47×10^5	610	
		DMSO	5.52×10^5	543	
		DMSO	2.70×10^5	425	
		DMSO	1.46×10^5	334	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Universal constant Θ	–	–	2.1×10^{21}	(15)
			3.6×10^{21}	(16)
Length of Kuhn statistical segment	Å	Aqueous, viscosity	21.1	(10)
		Aqueous, sedimentation	17.3	(10)
		DMSO	95	(10)
		Helical region, efficient bond length $b_0 = 1.33$ Å		(17)
		0.33 M KCl, viscosity	24	
		0.33 M KCl, sedimentation	26	
		0.2 M KOH, viscosity	74	
		0.2 M KOH, sedimentation	70	
		Nonhelical region, efficient bond length $b_0 = 4.41$ Å		(17)
		0.33 M KCl, viscosity	90	
		0.33 M KCl, sedimentation	86	
		0.2 M KOH, viscosity	240	
		0.2 M KOH, sedimentation	230	
Glass transition temperature T_g	K	Extrapolation data from substituted amylose	317	(18)
Melting temperature T_m	K	Extrapolation data from substituted amylose	527	(18)
Pyrolysis		Acidic catalyst, 79–120°C, 3–8 h	White dextrins	(19)
		Acidic catalyst, 150–270°C, 6–18 h	Yellow or canary dextrins	
		220°C, 10–20 h	British gums	
Pyrolysis weight loss	%	Amount (mg) / Temp. range		(20)
		80 / 240–265	10	
		265–300	59	
		100 / 300–350	11	
		240–265	10	
		265–300	58	
		300–350	12	
Enthalpy of hydration	kJ mol^{-1}	50–95°C, V_h (helix diameter, 13.7 Å) $\leftrightarrow H_2O + V_a$ (helix diameter, 13.0 Å)	43.5	(21)

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Specific rotation $[\alpha]$	Degree	Solvent	λ *(nm)*		
		Water	135	+200	(22)
			546	+232, 236	(23)
		0.5 M KCl	134	+201	(22)
			546	+200	(11)
		8 M urea	132	+200	(22)
		1 M NaOH	132	+162	(22)
		DMSO	210	+175	(22)
			546	+225, 226	(23)
			546	+171	(11)
		Formamide	546	+238, 239	(23)
		Ethylenediamine	546	+191, 195	(23)
		Hexamethylphosphoramide	546	+210, 212	(23)
		1 N KOH	546	+156	(11)
		0.5 N KOH	546	+174	(11)
Refractive index n_2^{46}	–	–		1.5198	(24)
Refractive index increment dn/dc	ml g^{-1}	DMSO, $\lambda = 436$ nm		0.0676 ± 3%	(11)
		DMSO, $\lambda = 546$ nm		0.0659 ± 3%	(11)
		1 N KOH		0.146	(25)
Sedimentation coefficient	Svedberg	Ultracentrifugation		10.2	(26)
		Source			(27)
		Rongotea		5.0 ± 0.2	
				5.2 ± 0.5	
				4.5 ± 0.1	
		Crossbow		2.6 ± 0.4	
				3.2 ± 0.1	
		Aotea		3.3 ± 0.1	
		Karamu		4.0 ± 0.7	
		Hilgendorf		5.7 ± 0.9	
				2.9 ± 0.6	
Segment mobility *m*s	–	Ultracentrifugation		0 (rigid)	(26)
Segment size l_m	Å	Ultracentrifugation		1.3	(26)
Surface tension	mN m^{-1}	–		37	(28)

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PROPERTY	UNITS	CONDITIONS		VALUE		REFERENCE
Tensile strength	MPa	50% relative humidity, 72°F				(29)
		Source	DP	Dry ($\times 10^{-2}$)	Wet ($\times 10^{-3}$)	
		Tapioca	2,110	6.08	1.3	
		White potato	1,610	5.79	2.1	
		Wheat	1,230	6.47	1.5	
		Sweet potato	1,215	6.27	2.2	
		Tapioca	1,205	6.86	1.8	
		Tapioca	915	7.06	1.9	
		Corn	820	7.15	2.0	
		Corn	505	6.66	1.0	
		Corn	435	6.96	0.2	
		Corn	420	7.25	0.6	
		Corn	400	7.45	1.0	
		Corn	310	5.19	0.5	
		Corn	265	6.47	—	
		Corn	230	1.86	—	
Elongation at break	%	50% relative humidity, 72°F				(29)
		Source	DP	Dry	Wet	
		Tapioca	2,110	13	39	
		White potato	1,610	9	57	
		Wheat	1,230	13	19	
		Sweet potato	1,215	14	42	
		Tapioca	1,205	18	38	
		Tapioca	915	14	18	
		Corn	820	13	15	
		Corn	505	6	6	
		Corn	435	7	5	
		Corn	420	8	5	
		Corn	400	10	6	
		Corn	310	6	4	
		Corn	265	9	—	
		Corn	230	1	—	
Tear strength	g	50% relative humidity, 72°F				(29)
		Source	DP			
		Tapioca	2,110	8		
		White potato	1,610	10		
		Wheat	1,230	10		
		Sweet potato	1,215	9		
		Tapioca	1,205	8		
		Tapioca	915	—		
		Corn	820	8		
		Corn	505	6		
		Corn	435	7		
		Corn	420	4		
		Corn	400	7		
		Corn	310	5		
		Corn	265	3		
		Corn	230	—		

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Permeability constant	mol cm^{-1} s^{-1} mm Hg^{-1}	Water at 25°C			(30)
		Relative humidity			
		1–53%		3.1 ± 10^{-11}	
		29–1%		1.5 ± 10^{-10}	
		1–100%		2.7 ± 10^{-10}	
		Organic vapor	Vapor pressure (cm Hg) at 35°C		(30)
		Methanol	20.4	2.5 ± 10^{-12}	
		Ethanol	10.4	5.8 ± 10^{-14}	
		1-Propanol	3.74	8.6 ± 10^{-14}	
		1-Butanol	1.31	2.5 ± 10^{-13}	
		Acedic acid	2.67	5.6 ± 10^{-14}	
		Ethyl acetate	16.5	4.4 ± 10^{-14}	
		Acetone	34.6	3.4 ± 10^{-14}	
		Carbon tetrachloride	17.6	1.6 ± 10^{-14}	
		Benzene	14.8	6.3 ± 10^{-14}	
		Benzaldehyde	0.16	8.0 ± 10^{-13}	
		Gas at 25°C			(30)
		Air		0	
		Oxygen		0	
		Nitrogen		0	
		Carbon dioxide		2.6 ± 10^{-16}	
		Ammonia		1.1 ± 10^{-12}	
		Sulfur dioxide		7.8 ± 10^{-14}	

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Bisphenol-A polysulfone

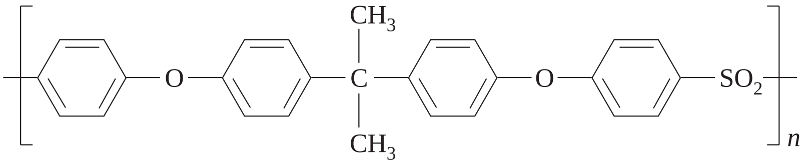
TAREK M. MADKOUR

ACRONYM, TRADE NAMES PSF, Udel P1700 and P3500 (Amoco)

CLASS Poly(ether sulfones)

SYNTHESIS Polycondensation

STRUCTURE



MAJOR APPLICATIONS Medical and household appliances that are sterilizable by hot air and steam such as corrosion-resistant piping. Also used in electric and electronic applications and as membranes for reverse gas streams and gas separation.

PROPERTIES OF SPECIAL INTEREST High-performance thermoplastic of relatively low flammability. Amorphous, high-creep resistance and stable electrical properties over wide temperature and frequency ranges. Transparent with good thermal and hydrolytic resistance. High alkaline stability.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	442.53	–
Infrared bands (frequency)	cm^{-1}	Group assignments		(1, 2)
		SO_2 scissors deformation	560	
		Aromatic ring bend	690	
		Para out-of-plane aromatic CH wag	834	
		Para in-plane aromatic CH bend	1,014	
		Para in-plane aromatic CH bend	1,105	
		SO_2 symmetric stretch	1,151	
		SO_2 symmetric stretch	1,175	
		Aryl-O-aryl C–O stretch	1,244	
		SO_2 asymmetric stretch	1,294	
		SO_2 asymmetric stretch	1,325	
		CH_3 symmetric (umbrella) deformation	1,365	
		Para aromatic ring semicircle stretch	1,410	
		Para aromatic ring semicircle stretch	1,490	
		Para aromatic ring semicircle stretch	1,505	
		Para aromatic ring quadrant stretch	1,585	

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Bisphenol-A polysulfone

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Infrared bands (frequency)	cm^{-1}	Group assignments		(1, 2)
		CH_3 symmetric stretch	2,875	
		CH_3 asymmetric stretch	2,970	
		Aromatic CH stretches	3,000–3,200	
Thermal expansion coefficient	K^{-1}	1 atm and 20°C	2.1×10^4	(3)
Isothermal compressibility	bar^{-1}	20°C	2.2×10^5	(3)
Density	$g\,cm^{-3}$	—	1.24	(4)
Solubility parameter	$(MPa)^{1/2}$	—	20.26	(5)
Glass transition temperature	K	Forced oscillation dynamic-mechanical analysis	459	(6)
Sub-T_g transition temperature	K	β-relaxation temperature	358	(6)
		γ-relaxation temperature	193	
Heat deflection temperature	K	(1.82 MPa)	447	(7)

Mechanical properties[4,7,8]

Property	Units	Resin		
		Neat resin	30% glass fiber reinforced	30% carbon fiber reinforced
Tensile modulus	MPa	2,482	—	—
Tensile strength	MPa	69.0	120	190
Maximum extensibility $(L/L_0)_r$	%	3.0	2.31	1.02
Flexural modulus	MPa	2,758	6,747	13,069
Flexural strength	MPa	103	208	244
Notched Izod impact strength	$J\,m^{-1}$	80.4	400	118
Unnotched Izod impact strength	$J\,m^{-1}$	—	1,049	456
Hardness	Shore D	69	85	87

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PROPERTY	UNITS	CONDITIONS	VALUE			REFERENCE
WLF parameters: C_1 and C_2	—	—	$C_1 = 15.1$ $C_2 = 49.0$			(9)
Dielectric strength	$MV\,m^{-1}$	—	14.6			(4)
Resistivity	ohm cm	—	5×10^{16}			(4)
Thermal conductivity k	$W\,m^{-1}\,K^{-1}$	—	0.26			(11)
Melt index	$g\,(10\,min)^{-1}$	—	6.5			(4)
Water absorption	%	24 h	0.3			(4)
Intrinsic viscosity	$cm^3\,g^{-1}$	25°C in chloroform	End group			(12)
			NH_2	Cl	t-Butyl	
		Mol. wt. = 5,720	0.16	0.16	—	
		Mol. wt. = 9,934	0.23	—	0.24	
		Mol. wt. = 17,500	0.29	—	0.30	
		Mol. wt. = 21,230	0.34	—	0.33	

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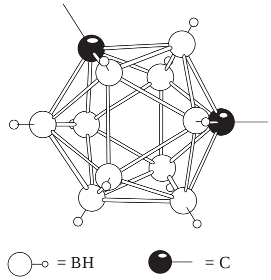
Carboranе-containing polymers

EDWARD N. PETERS AND R. K. ARISMAN

ACRONYM, TRADE NAME SiB, Dexsil (Olin Corp.)

CLASS Cage structure polymers; D_n-carborane siloxanes

STRUCTURE $[-Si(CH_3)_2CB_{10}H_{10}CSi(CH_3)_2-O-\{Si(CH_3)_2-O-\}_{n-1}-]$, where $CB_{10}H_{10}C$ is as follows:



MAJOR APPLICATIONS Liquid phase in gas chromatography. High-temperature elastomer used to formulate gaskets, O-rings, and wire coatings. Can be fabricated like conventional silicones.

PROPERTIES OF SPECIAL INTEREST Elastomeric. Very high thermal stability. Outstanding flame resistance.

IR (characteristic absorption frequencies)* [(1)]

n	Assignment				
	C–H	B–H	CH_3	Si–O	Si–C
1	2,963; 2,904	2,600	1,410; 1,262	1,090	800
3	2,960; 2,900	2,595	1,411; 1,263	1,090; 1,048	801
4	2,963; 2,904	2,600	1,411; 1,260	1,095; 1,047	800
5	2,963; 2,904	2,594	1,410; 1,263	1,065; 1,030	800

*Wave numbers (cm^{-1}) for $[-Si(CH_3)_2CB_{10}H_{10}CSi(CH_3)_2-O-\{Si(CH_3)_2-O-\}_{n-1}-]$.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
NMR	Proton NMR in $CDCl_3$			
	At 60 MHz			(2)
	at 100 MHz			(1)
Solvents	–	At 25°C	Diethyl ether	(2)
			Chlorobenzene	(3)
Nonsolvents	–	At 25°C	Methanol	(3)
Mark Houwink parameters: *K* and *a*	$K = ml\,g^{-1}$ a = None	–	$K = 1.02 \times 10^{-4}$ $a = 0.72$	–

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PROPERTY	UNITS	CONDITIONS*				VALUE	REFERENCE
Density	$g\,cm^{-3}$	R_1	R_2	R_3	n		(4)
		CH_3	CH_3	CH_3 (67) Phenyl (33)	2	1.074	
		CH_3	Phenyl (33) CH_3 (67)	Phenyl (33) CH_3 (67)	2	1.123	
Glass transition temperature	K	R_1	R_2	R_3	n		
		CH_3	CH_3	–	1	298	(5)
		CH_3	CH_3	CH_3	2	243	(5)
						223	(5)
		CH_3	CH_3	CH_3	3	205	(7)
		CH_3	CH_3	CH_3	4	203	(7)
		CH_3	CH_3	CH_3	5	185	(7)
		CH_3	CH_3	Phenyl	2	261	(6)
		CH_3	CH_3	CH_3 (33) Phenyl (67)	2	251	(6)
		CH_3	CH_3	CH_3 (67) Phenyl (33)	2	236	(6)
		CH_3	Phenyl	Phenyl	2	295	(6)
		CH_3	Phenyl (33) CH_3 (67)	Phenyl (33) CH_3 (67)	2	248	(6)
		CH_3	Phenyl (24) CH_3 (76)	Phenyl (24) CH_3 (76)	2	240	(6)
		$CH_2CH_2CF_3$	$CH_2CH_2CF_3$	–	1	301	(8)
		CH_3	CH_3	$CH_2CH_2CF_3$	2	244	(9)
		$CH_2CH_2CF_3$	$CH_2CH_2CF_3$	CH_3	2	261	(9)
		$CH_2CH_2CF_3$	$CH_2CH_2CF_3$	$CH_2CH_2CF_3$	2	270	(9)
		$CH_2CH_2CF_3$	$CH_2CH_2CF_3$	$CH_2CH_2CF_3$	3	270	(8)
Melting temperature	K	R_1	R_2	R_3	n		
		CH_3	CH_3	–	1	513	(5)
		CH_3	CH_3	CH_3	2	339	(5)
						341, 363	(5)
		CH_3	CH_3	CH_3	3	313	(7)
Tensile modulus†	MPa	R_1	R_2	R_3	n		
		CH_3	CH_3	CH_3 (33) Phenyl (67)	2	3.45	(10)
		CH_3	Phenyl (33)	Phenyl (33)	2	2.97	(11)
Tensile strength†	MPa	R_1	R_2	R_3	n		
		CH_3	CH_3	CH_3 (33) Phenyl (67)	2	3.58	(10)
		CH_3	Phenyl (33) CH_3 (67)	Phenyl (33) CH_3 (67)	2	5.10	(11)

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PROPERTY	UNITS	CONDITIONS*				VALUE	REFERENCE
Maximum extensibility†	%	R_1	R_2	R_3	n		
		CH_3	CH_3	CH_3 (33) Phenyl (67)	2	130	(10)
		CH_3	Phenyl (33) CH_3 (67)	Phenyl (33) CH_3 (67)	2	220	(11)
Dielectric constant ε†		R_1	R_2	R_3	n		(12)
		CH_3	CH_3	CH_3	2	2.27	
		CH_3	CH_3	CH_3	4	5.92	
Loss factor $\tan\delta$†		R_1	R_2	R_3	n		(12)
		CH_3	CH_3	CH_3	2	0.0053	
		CH_3	CH_3	CH_3	4	0.52	
Pyrolyzability	%	800°C in argon					(7)
		R_1	R_2	R_3	n		
		CH_3	CH_3	–	1	20	
		CH_3	CH_3	CH_3	2	29	
		CH_3	CH_3	CH_3	3	36	
		CH_3	CH_3	CH_3	4	47	
		CH_3	CH_3	CH_3	5	48	
		800°C in argon					(6)
		R_1	R_2	R_3	n		
		CH_3	CH_3	Phenyl	2	4	
		CH_3	CH_3	CH_3 (33) Phenyl (67)	2	5	
		CH_3	CH_3	CH_3 (67) Phenyl (33)	2	6	
Flammability							
Oxygen index	%	R_1	R_2	R_3	n		(10)
		CH_3	CH_3	Phenyl	2	62	
TGA: 5% weight loss temperature in air	K	R_1	R_2	R_3	n		
		CH_3	CH_3	–	1	>973	(13)
		CH_3	CH_3	CH_3 (67) Phenyl (33)	2	1,023	(6)
		CH_3	CH_3	CH_3 (33) Phenyl (67)	2	>1,073	(6)
		CH_3	Phenyl	Phenyl	2	>1,073	(6)
		CH_3	CH_3	CH_3	3	793	(2)

*For the polymer series: $[-Si(R_1)(CH_3)CB_{10}H_{10}CSi(R_1)(CH_3)-O-\{Si(R_2)(R_3)-O-\}_{n-1}-]$

†Mechanical properties: for resins with 30 phr trimethylsilated amorphous silica, 2.5 phr ferric oxide, and cured with 2.5 phr dicumyl peroxide.

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Synthesis

n	Solvent	Catalyst	Temp. (°C)	Monomers	Reference
1	—	$FeCl_3$	175–225	1,7-bis-(methoxydimethylsilyl)-*m*-carborane 1,7-bis-(chlorodimethylsilyl)-*m*-carborane	(14)
2	Chlorobenzene	—	−10	1,7-bis-(hydroxyldimethyl)-*m*-carborane bis(N-phenyl-N′-tetramethyleneureido)silane	(3)
3	Diethyl ether/THF/water	—	25	1,7-bis-(chloro-1,1,3,3-tetramethyldisilyl)-*m*-carborane	(2)

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Carboxylated ethylene copolymers, metal salts (ionomers)

RUSKIN LONGWORTH

TRADE NAME Surlyn (Du Pont)

CLASS Chemical copolymers; ethylene copolymers

STRUCTURE $-(CH_2-CH_2)_n-[CH_2-C(CH_3)(Co_2Na^+)]_m-$
$[-CH_2-CH_2-CCH_3(CO_2-H)]_l-$
Typically, if $n+m+l=100$, then $m+l$ is 1–5.

GENERAL INFORMATION The Surlyn brand of ionomers consists of copolymers of ethylene with methacrylic acid, partially or wholly neutralized with a variety of metals, including sodium, zinc, and lithium.[1,2] The neutralization process drastically increases the melt viscosity and decreases the solubility, making molecular weight determinations of the final product impossible. However, the metal ions can be removed by treatment with acids, and the unneutralized copolymer examined by methods similar to those used for low density polyethylene (LDPE) and copolymers thereof. In certain cases, the properties of the ionomer resemble LDPE; where applicable, these values are given in italics. About twenty grades of Surlyn plastics exist. Here we report on two representative samples: sodium (Na) neutralized and zinc (Zn) neutralized. Where experimental conditions are described by a ''D-'' number, these refer to test procedures of the American Society for Testing Materials.

MAJOR APPLICATIONS Moldings (e.g., golf ball covers, ski boots) and film (e.g., meat packaging, coextrusions).

Preparative techniques[1]

Method	Conditions
Free radical polymerization	Peroxide initiator, high pressure (>100 MPa)
Ceiling temperature	550 K
Comonomer	Methacrylic acid
Post-synthesis adducts	Sodium, lithium, zinc

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	28	—
Molecular weight (of acid comonomer)	$g\,mol^{-1}$	—	86	(1)
Tacticity	—	—	Random	—
Trans unsaturation	—	—	0.025/1,000C	(3)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Vinylidene unsaturation	–	–	0.15/1,000C	(3)
Short-chain branching	–	–	2/100C	(3)
Long-chain branching	–	–	1/1,000C	(3)
Molecular weight (M_w)	g mol^{-1}	–	500,000	(3)
Polydispersity	–	–	10	(3)
Morphology	–	Three phases	Semicrystalline PE Amorphous PE Ionic clusters (ionic comonomers with some PE)	(1)
IR (characteristic absorption frequencies)	cm^{-1}	Hydrogen-bonded hydroxyl Unionized carbonyl Carboxylate	2,650 1,700 1,560	(4)
Thermal expansion coefficient	K^{-1}	D-696 Na Zn	 5.9×10^{-5} 5.7×10^{-5}	(2)
Density	g cm^{3}	Na Zn Amorphous	0.95 0.94 0.855	(2) (2) (5)
Degree of crystallinity	%	Na; annealed 4 h at 348 K	30	(6)
Heat of fusion	kJ mol^{-1}	Na; annealed 4 h at 348 K	2.32	(6)
Density	g cm^{3}	Crystalline PE	1.014	(7)
Transition temperatures	K	Amorphous polyethylene Crystalline polyethylene (M.P.) Beta transition (amorphous hydrocarbon) Ionic transition (order-disorder)	148 373 253 331	(1)
Heat capacity	kJ K^{-1}	–	4.2–5.0	(2)
Deflection temperature	K	Vicat, D-1525 Na Zn	 337 346	(2)
Flex modulus	MPa	D-790, 298 K Na Zn	 350 130	(2)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile modulus	MPa	Secant modulus, D-882, 298 K		(8)
		Na	290	
		Zn	280	
Storage modulus (1 Hz, G')	MPa	Na		(1)
		193 K	1,000	
		273 K	330	
		295 K	205	
		334 K	30	
Loss modulus (1 Hz, G'')	MPa	Na		(1)
		193 K	25.9	
		273 K	32.3	
		295 K	20.9	
		334 K	6.2	
Tensile strength	MPa	D-638, 296 K		(2)
		Na	33.1	
		Zn	21.4	
Yield strength	MPa	D-638, 296 K		(2)
		Na	15.9	
		Zn	8.3	
Maximum elongation	%	Na	470	—
		Zn	500	
Flex modulus	MPa	D-790, 296 K		—
		Na	350	
		Zn	130	
Impact strength	$J\,m^{-1}$	D-250, notched Izod, 296 K		(2)
		Na	1.02×10^5	
		Zn	No break	
Tensile impact strength	$J\,m^{-2}$	D-1822S		(2)
		Na; 296 K	1,020	
		Na; 233 K	760	
		Zn; 296 K	925	
		Zn; 233 K	560	
Hardness	Shore D	Na	65	(2)
		Zn	54	
Entanglement molecular weight	—	—	15,000	(1)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Abrasion resistance	–	D-1630		(2)
		Na	370	
		Zn	170	
Index of refraction	–	Zn	1.49	(7)
Dielectric constant	–	Na; 1 kHz, 296 K	3.8	(9)
Dielectric loss	–	Na; 1 kHz, 296 K	4.0×10^{-3}	(9)
Strain-optical coefficient K_s	–	Na; maximum at 331 K	2.4×10^{-2}	(10)
Permeability	$m^3\ m\,s^{-1}\ m^{-2}\ Pa^{-1}$	Oxygen, 296 K		(7)
		Na	1.80×10^{-17}	
		Zn	2.00×10^{-17}	
	$g\ m\,s^{-1}\ m^{-2}\ Pa^{-1}$	Water vapor, 296 K; Na, Zn	7.00×10^{-12}	–
Viscosity	Pa s ($\times 10^4$)	Piston rheometer; shear rate = $1.30\,s^{-1}$		–
		Na at 393 K	5.18	
		Na at 413 K	2.85	
		Na at 433 K	1.61	
Melt index	$g\,s^{-1}$ ($\times 10^{-3}$)	D-1238-57-T, condition E		–
		Na, shear rate = $7.0\,s^{-1}$	4.7	
		Zn, shear rate = $4.0\,s^{-1}$	2.7	
Maximum use temperature (heat deflection temperature)	K	D-648, 455 kPa		(2)
		Na	317	
		Zn	313	
Flammability	$cm\,s^{-1}$	D-635		(2)
		Na	3.81	
		Zn	3.38	
Water absorption	wt%	Saturation, 296 K		(1)
		Na (3 mol% carboxylate)	11	
		Na (6 mol% carboxylate)	29	
Haze	%	D-1003		–
		Na	3.0	
		Zn	7.0	
Clarity	%	D-1746; Na, Zn	40–60	–
Elmendorf tear strength	$N\,mm^{-1}$	D-1922		–
		Na (MD, TD)	3.2	
		Zn (MD, TD)	20.0	

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Carboxylated ethylene copolymers, metal salts (ionomers)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Cost	US$ kg^{-1}	–	3.33–4.02	–
Important patent	Rees, R. W. *U.S. Patent* 3,264,272 (assigned to E. I du Pont de Nemours and Co.)			
Supplier	E. I. du Pont de Nemours and Co., Du Pont Polymers, Wilmington, Delaware 19898, USA			

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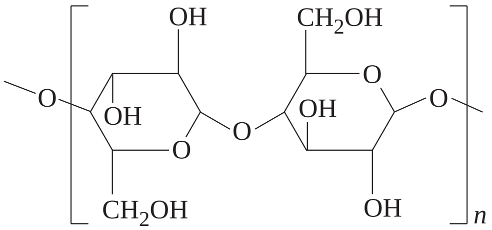
Cellulose

RACHEL MANSENCAL

ALTERNATIVE NAMES Rayon, cellophane, regenerated cellulose[1]

CLASS Carbohydrate polymers; polysaccharides

STRUCTURE



FUNCTIONS It is the basic structural material of the cell walls of all higher land plants and of some seaweeds.[2–8]

NATURAL SOURCES Wood (coniferous, deciduous), bamboo, cotton, hemp, straw, jute, flax, reed, sisal. Cellulose is isolated from the plant cell walls and is never in a pure form in nature. Always associated with lignin and hemicellulose.[2–4]

Source[4]	Cellulose (%)
Cotton	94
Hemp	77
Flax	75
Kapok	75
Sisal	75
Ramie	73
Jute	63
Wood (coniferous or deciduous)	50
Bamboo	40–50
Straw	40–50

BIOSYNTHESIS Depends on the system.[6–8]

COMMERCIAL USES Natural cellulose is used as fuel and lumber. Purified cellulose is employed for production of paper and textiles. Derivatives of cellulose are used in plastics, films, foils, glues, and varnishes. Most of the cellulose is used in paper and paperboard manufacture.[4]

EXTRACTION The separation process of cellulose from hemicellulose and lignine is by pulping. The two different kinds of pulping are mechanical and chemical.[2–4, 6]

PROPERTIES OF SPECIAL INTEREST Cellulose is the most abundant macromolecular material naturally occurring in plant cell walls. Semicrystalline natural polymer. Very difficult to dissolve.[2–7]

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Cellulose

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Average molecular weight	$g\,mol^{-1}$	–	$\approx 10_6$	(6)
Specific gravity	$g\,cm^{-3}$	In heptane	1.540	(4)
		In benzene	1.570	
		In water	1.604–1.609	
Cellulose fibril size	nm	Subelementary	1.5	(4)
		Elementary	3.5	
X-ray density	$g\,cm^{-3}$	Crystalline portion	1.590–1.630	(4)
		Amorphous portion	1.482–1.489	
Average crystallinity	%	Native	70	(4)
Optical refractive index	–	$n_D^{\parallel}$	1.618	(4)
			1.599	
			1.600	
			1.595	
		$n_D^{\perp}$	1.543	
			1.532	
			1.531	
			1.534	
Solubility	–	Water, organic solvent, dilute acid, alkalies	Insoluble	(5)
		Cuprammonium hydroxide	Soluble (complex formation)	
		Cupriethylenediamine hydroxide		
		Cadmium ethylene diamine hydroxide		
		Iron sodium tartrate complex		
Solubility parameters	$(MPa)^{1/2}$	–	32.02	(1)

Unit cell dimensions[2, 8, 9]

Isomer	Lattice	Space group	Monomers per unit cell	Cell dimension* (Å) a	b (fiber axis)	c	Cell angles (degrees) γ
Cellulose I	monoclinic	2_1	2 (parallel arrangement of the chains)	9.35	10.3	7.9	96.0
Cellulose II	monoclinic	2_1	2 (antiparallel arrangement of the chains)	8.0	10.3	9.0	117

*For ramie and cotton.

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Polymorphs	Cellulose I, II, III, IV, III-1, III-2, IV-1, IV-2			(2)
Degree of crystallinity	%	Determined by X-ray diffraction		
		Type of cellulose		
		Cellulose (*valonia ventricosa*)	0.68	(5, 10)
		Different wood pulps	0.62–0.70	(5, 10, 11)
		Ramie	0.60–0.71	(5, 10, 11)
Thermal conductivity λ_c	$W\,m^{-1}\,K^{-1}$	Cotton, 293 K	0.071	(1, 5, 13)
		Rayon	0.054–0.07	(1, 5, 14)
		Sulfite pulp, wet	0.8	(1, 5, 15)
		Sulfite pulp, dry	0.067	(1, 5, 15)
		Laminated kraft paper	0.13	(1, 5, 16)
		Different papers, 303–333 K	0.029–0.17	(1, 5, 17)
Thermal expansion coefficient (linear expansion) for different papers	K^{-1} ($\times 10^{-6}$)	Machine direction	2–7.5	(5, 18)
		Cross-machine direction	7.9–16.2	
Specific heat	$J\,g^{-1}\,K^{-1}$	–	1.22	(4)
Heat of combustion	$kJ\,g^{-1}$	–	17.43	(4)
Dielectric constant	–	Crystalline portion	5.7	(4)
Isolation resistance	ohm cm	–	2×10^4	(4)
Insulating value	$kV\,cm^{-1}$	–	500	(4)
Thermal decomposition	K	–	523	(4)
Start of thermal degradation	K	Linters	498	(19)
		Bleached sulfite pulp	498	(19)
		Kraft pulp	513	(19)
		Filter paper (under nitrogen)	493	(20)
Fast endothermal degradation	K	Linters	≈573	(19)
		Bleached sulfite pulp	≈603	(19)
		Cotton (under nitrogen)	563	(4)
		Cellulose powder (thermogravimetry)	563	(21, 22)
Ignition temperature	K	Cotton	663, 673	(14, 23)
		Viscose rayon	693	(23)
Self ignition temperature	K	Cotton	673	(4)

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
External ignition temperature	K	Cotton	623		(4)
Maximum flame temperature	K	Cotton			
		19% O_2	1,123		(4, 5)
		25% O_2	1,323		(5, 24)
Heat capacity	$kJ\,kg^{-1}\,K^{-1}$	Cellulose	1.34		(5, 25)
		Cotton	1.22		(5, 26)
		Mercerized cotton	1.235		(5, 26)
		Ramie	1.775		(5, 27)
		Flax	1.344–1.348		(5, 28)
		Hemp	1.327–1.352		(5, 28)
		Jute	1.357		(5, 28)
		Viscose rayon	1.357		(5, 28)
		Paper	1.17–1.32		(5)
Heat of crystallization	$kJ\,kg^{-1}$	Cellulose I	121.8		(5)
		Cellulose II	134.8		(5)
Heat of recrystallization	$kJ\,kg^{-1}$	Amorphous cellulose → Cellulose I	41.9		(5, 29)
Heat of transition	$kJ\,kg^{-1}$	Cellulose I → Cellulose II	38.1		(5, 30)
Heat of formation	$kJ\,kg^{-1}$	–	5949.7		(5, 31)
Heat of solution of dry material	$kJ\,kg^{-1}$	Cotton in cupriethylendiamine	108.0		(5, 32)
		Cotton in Et_3PhNOH	142.5		(5, 33)
		Rayon in Et_3PhNOH	95.5		(5, 34)
		Cellulose II in Et_3PhNOH	182.7		(5, 33)
Yields of scission $G(S)$	$\mu mol\,J^{-1}$	Electron beam or γ-irradiation	11		(5, 35)
Glass transition temperature	K	–	503		(5)
			493–518		
Secondary transition	K	–	292–296		(5)
			298		
Tensile strength	MPa		Dry	Wet	(4)
		Ramie	900	1,060	
		Cotton	200–800	200–800	
		Flax	824	863	
		Viscose rayon	200–400	100–200	
		Viscose rayon, highly oriented	610	520	
		Cellulose acetate	150–200	100–120	

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Relative wet/dry strength	%	Ramie	117		(4)
		Cotton	105		
		Flax	105		
		Viscose rayon	50		
		Viscose rayon, highly oriented	86		
		Cellulose acetate	65		
Extension at break	%		Dry	Wet	(4)
		Ramie	2.3	2.4	
		Cotton	16–12	6–13	
		Flax	1.8	2.2	
		Viscose rayon	8–26	13–43	
		Viscose rayon, highly oriented	9	9	
		Cellulose acetate	21–30	29–30	
Elastic modulus	MPa	Native flax	78,000–108,000		(4)
		Native hemp	59,000–78,000		
		Native ramie	48,000–69,000		
		Mercerized ramie	80,000		
		Oriented rayon	33,000		
		Cellulose acetate film	4,000		

Void system determination by X ray small angle scattering

Cellulose	Relative internal surface ($Å^2\ Å^{-3}$)	Specific internal surface ($m^2\ g^{-1}$)	Conditions	Reference
Microcrystalline	0.09273	2.93	Average values	(5, 36, 37)
	0.0714	1.74		
Microfine	0.07232	1.10	—	(5)
	0.12800	2.08		

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Permeability to gases	—	Cellulose, 25°C, pressure not specified	H_2, N_2, O_2, CO_2, SO_2, H_2S, NH_3	(5, 38)
Density	$g\ cm^{-3}$	Cellulose I	1.582–1.630	(5, 39–41)
		Cellulose II	1.583–1.62	(5, 40)
		Cellulose IV	1.61	(5)
		Cotton	1.545–1.585	(5, 42–44)
		Ramie	1.55	(40)
		Flax	1.541	(5)
		Hemp	1.541	(5)
		Jute	1.532	(5)
		Wood pulps	1.535–1.547	(5, 40, 45)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of adsorption of water, ΔH_{ads}	$J g^{-1}$	Cotton, 25°C	384	(4)
		Holocellulose, 25°C	344	
		Bleached sulfite pulp, 20°C	348	
		Cellophane, 25°C	358	
		Viscose rayon, 25°C	397	
IR (characteristic absorption frequencies)	cm^{-1}	Cellulose I	3,125–3,660; 3,375; 3,275; 2,970; 2,960; 2,945; 2,900; 1,760; 1,730–1,740; 1,550–1,650; 1,035; 1,025; 1,015; 700; 740	(4)
		Cellulose II	6,770; 3,464–3,490; 3,444–3,450; 3,374–3,394	

Optical configuration parameters[1,46]

Cellulose	Delta alpha (A^3)	Diluent
Cellulose acetate DS = 2.4	0	Pyridene
Cellulose benzoate DS = 3.0	−617	Dimethylformamide
Cellulose nitrate DS = 1.9	−62	Cyclohexanone
Cellulose nitrate DS = 1.9	149	Dioxane

*DS = Degree of substitution.

Mark-Houwink parameter*: K and a

Solvent	Temp. (°C)	$K_m \times 10^2$ (ml g^{-1})	a	K'_m (ml g^{-1})†	Viscosity range $[\eta] \times 10^{-2}$ (ml g^{-1})	Method of calibration	Reference
Cuoxam[a]	20	0.308	1.0	0.5	0.9–9	Osmotic	(5, 47)
	25	11.3	0.657	3.19	0.2–4	Visco[d]	(5, 48)
	25	10.1	0.661	2.91	0.2–4	Visco[d]	(5, 48)
Cuene[b]	25	–	0.905	1.33	1–21.4	Visco[d]	(5, 49, 50)
	25	0.498	1.0	0.807	2.4–21.4	–	(5, 49, 50)
Cadoxene[c]	25	–	1.0	0.435	0.5–7.5	Visco[d]	(5, 51)

*For cellulose; from osmotic measurements on fractionated samples.
†K'_m is relating intrinsic viscosity and degree of polymerization
[a]Cuoxam: cuprammonium hydroxide.
[b]Cuene: cupriethylenediamine.
[c]Cadoxene: cadmiumethylenediamine.
[d]Visco: viscosimetric comparison.

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Martin coefficient K'	–	Cellulose		(5)
		Solvent		
		Cuene*	0.13–0.15	
		Cuoxam†	0.1303	
			0.112	
Huggins coefficient K''	–	Cellulose		(5)
		Solvent		
		Cuoxam†	0.37	
		Cadoxene‡	0.26–0.39	
Schulz-Blaschke coefficient K'''	–	Cellulose		
		Solvent		
		Cuene*	0.33	(5)
		Cuoxam†	0.29	(5, 52)
			0.1552	(5, 53)
			0.287	(5, 52)
		Cadoxene‡	0.280	(5)
Second virial coefficient A_2	mol cm^3 g^{-2} ($\times 10^4$)	Cellulose	16.1	(5)
		Hydrolyzed linters; cadmium ethylene diamine solvent; 25°C; $M = (225–945) \times 10^{-3}$ g mol^{-1}; light scattering		
		Sulfite pulp; $M = 215 \times 10^{-3}$ g mol^{-1}; light scattering	12.1	
Sedimentation coefficients s_0	s $\times 10^{13}$	Cellulose in solution		
		Cuene*; 25°C		(1, 5)
		$M = 175 \times 10^{-3}$ g mol^{-1}	5.5	
		$M = 9.5 \times 10^{-3}$ g mol^{-1}	8.3	
		Cadoxene‡; 12°C		(1, 5, 54)
		$M = 33.6 \times 10^{-3}$ g mol^{-1}	1.25	
		$M = 24.5 \times 10^{-3}$ g mol^{-1}	1.13	
		$M = 18.8 \times 10^{-3}$ g mol^{-1}	1.04	
		$M = 10.1 \times 10^{-3}$ g mol^{-1}	0.74	
Diffusion coefficients D_0	cm^3 s ($\times 10^7$)	Cellulose in solution		(1, 5)
		Cuene*; 25°C		
		$M = 175 \times 10^{-3}$ g mol^{-1}	1.2	
		$M = 9.5 \times 10^{-3}$ g mol^{-1}	0.95	
Frictional ratios v_2	cm^3 g^{-1}	Cellulose in solution; cuene*; 25°C; $M = 175 \times 10^{-3}$ g mol^{-1}	0.65	(1, 5)
Specific resistance ρ	ohm cm	–	10^{18}	(5, 55)
Dielectric constant ε	–	106 kHz	5.5–8.1	(5, 56)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric loss factor tan δ	—	20°C, 0.1 kHz	0.015	(5)
		20°C, 1 kHz	0.02	
		20°C, 10 kHz	0.03	
		20°C, 10^2 kHz	0.045	
		20°C, 10^3 kHz	0.065	
		20°C, 10^4 kHz	0.08	
		20°C, 10^5 kHz	0.07	
Dielectric strength	kV mm^{-1}	Dry (native cellulose fiber)	50	(5, 57)
Zeta-potential	mV	Fines from filter paper, Whatman No. 1	21.0	(5, 58)
Surface tension	mN m^{-1}	Contact angle method, at 20°C		(5, 59)
		Cellulose regenerated from cotton	42	
		Cellulose regenerated from wood pulp	36–42	

*Cuene: cupriethylenediamine.
†Cuoxam: cuprammonium hydroxide.
‡Cadoxene: cadmiumethylenediamine.

Specific refractive index increment in dilute solution, dn/dc (ml g^{-1})

Solvent	$\lambda_0 = 436$ nm	$\lambda_0 = 546$ nm	Temp. (°C)	Reference
Acetone	0.111	—	25	(1, 60)
Cadoxene*	0.186	0.183	25	(1, 12, 54)
Cadoxene*, (5% Cd)/water (1:1 vol)	0.190	0.189	25	(1, 61)
0.237 M Cd	0.1317	0.1927	25	(1, 62)
Cuoxam† 0.205 M Cu	0.117	0.233	25	(1, 5)
Cuoxam† 0.0518 M Cu	0.1352	0.2574	25	(1, 62)
FeTNa	0.110	0.245	25	(1, 63)

*Cadoxene: cadmiumethylenediamine.
†Cuoxam: cuprammonium hydroxide.

Microbial biodegradation[5]

Class	Microorganism
Bacteria	*Cellvibro gilvus*
	Clostridium thermocellum
	Bacteroides succinogenus
	Ruminococcus albus
	Psudonomas fluorescence var *cellulosa*
	Sporocytophaga myxococcides

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Class	Microorganism
Fungi	*Coriolus vesicolor*
	Phanerochaete chrysosprium
	Irpex lacteus
	Schizophyllum commune
	Fomess annonus
	Stereum sanguinolentum
	Peurotus ostreatus
	Polyporrus schweinitzii
	Poria placenta
	Poria vailantii
	Coniophora cerebella
	Tyromyces palustris
	Serpula lacrymans
	Lentinus lepideus
	Chaetomium globosum
Ascomycetes and fungi imperfecti	*Chaetomiium thermophile*
	Trichoderma viride
	Trichoderma reesei
	Trichoderma koningii
	Penicillium funicolosum
	Fusarium solani
	Aspergillus aculeatus
	Aspergillus niger
	Sporotrichum thermophile
	Myrothecium verrucaria

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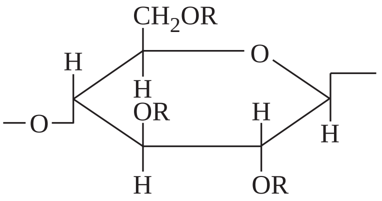
Cellulose acetate

YONG YANG

ACRONYM CA

CLASS Carbohydrate polymers

STRUCTURE



(R is $COCH_3$ or H)

MAJOR APPLICATIONS Textile fibers, cigarette filters, plastics for molding and extrusion, films for photography and recording tape, sheeting, lacquers, protective coatings for paper, metal, and glass, adhesive for photographic film, membranes.

PROPERTIES OF SPECIAL INTEREST White, ordorless, nontoxic, wide range of solvent tolerances.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	g mol^{-1}	Degree of substitution (DS) = 3.0	288.25	–
Preparation (acetylation)	Cellulose + Acetic anhydride $\xrightarrow[-H_2O]{[H_2SO_4]/\Delta}$ Cellulose acetate			(1)
IR (characteristic absorption frequencies)	cm^{-1}	Assignment		(2–4)
		(OH) stretching	~3,400	
		(CH_3) asymmetric stretching	~2,950	
		(CH_3) symmetric stretching	~2,860	
		(C=O) stretching	~1,750	
		((CH_3) asymmetric deformation	~1,432	
		(CH_3) symmetric deformation	~1,370	
		Acetate C–C–O stretching	~1,235	
		(C–O) stretching	~1,050	
		Structural factor	~603	
NMR	–	^{13}C and ^{1}H	–	(5)
Thermal expansion coefficient	K^{-1}	Sheet	$(10–15) \times 10^{-5}$	(6)
Density	g cm^{-3}	–	1.29–1.30	(1)

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Cellulose acetate

Solvents and nonsolvents

DS	Solvent	Nonsolvent	Reference
0.6–0.8	Water	–	(7)
1.3–1.7	2-Methoxyethanol	Acetone, water	(7–9)
2–2.5	Acetic acid*, acetone*, acrylic acid*, aniline, benzyl alcohol, cyclohexanone, *p*-chlorophenol*, *m*-cresol*, dichloroacetic acid*, diethanolamine, difluoroacetic acid*, *N,N*-dimethylacetamide*, dimethylformamide*, 1,5-dimethyl-2-pyrrolidone*, dimethylsulfoxide*, 1,4-dioxane*, ethylene glycol ether, ethyl acetate, formic acid*, glycol sulfite*, hexafluoroisopropanol*, methyl acetate, *n*-methylpyrrolidone-2*, naphthol*, nitrobenzene/ethyl acetate, nitromethane*, phenol*, phosphoric acid*, pyridine*, tetrafluoro-*n*-propanol*, tetrafluoroisopropanol*, trifluoroacetic acid*, trifluoroethanol*	Hydrocarbons, aliphatic ethers, weak mineral acids	(7–9)
3.0	Acetic acid* acetone*, acetone/water (8:2), aniline*, chloroform, *m*-cresol*, dichloroacetic acid*, dichloromethane*, *N,N*-dimethylacetamide*, dimethylformamide*, dimethylsulfoxide*, 1,4-dioxane*, ethyl acetate, ethylene carbonate, ethylene glycol ether acetates, methyl acetate*, methylene chloride, methylene chloride/ethanol (8:2), nitromethane*, 3-picoline*, 4-picoline*, *n*-propyl acetate*, pyridine*, tetrachloroethane*, tetrahydrofuran, trifluoroacetic acid*, trifluoroethane, trifluoroethanol*	Aliphatic hydrocarbons, benzene, dichloroethane, chlorobenzene, *o*-chlorotoluene, ethanol, aliphatic ethers, weak mineral acids	(7–9)

*Forms liquid crystalline mesophase.

Solubility parameter δ

DS	Solvent	Method	δ [(MPa)$^{1/2}$]	Reference
1.9	–	Heat of solution/solvation	27.2	(10)
2.3	Acetone	Osmotic pressure	23.0	(11)
	m-Cresol	Osmotic pressure	21.2	
	Dioxane	Osmotic pressure	22.5	
	Methyl acetate	Osmotic pressure	22.6	
	α-Picoline	Osmotic pressure	21.9	
	β- Picoline	Osmotic pressure	22.4	
	γ- Picoline	Osmotic pressure	22.0	
	Pyridine	Osmotic pressure	22.5	
2.3	–	Gel swelling	24.7	(12)
2.4	–	Intrinsic viscosity maximum	21.7	(13)
2.5	–	Heat of solution/solvation	27.8	(10)
2.8	–	Gel swelling	27.8	(12)

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Polymer-liquid interaction parameters χ (ϕ_2)[11, 14–18]

Solvent	DS	Temp. (K)	$\chi(0)$	$\chi(0.2)$	$\chi(0.4)$	$\chi(0.6)$
Acetone	2.3	298–318	0.44	—	—	—
	2.5	303	—	0.30	0.51	—
Acetic acid	2.3	298–318	—	0.40	—	—
Aniline	2.3	298–318	—	0.375–0.34	—	—
Chloroform	3.0	298	0.34	—	—	—
	3.0	303	—	0.36	0.45	0.51
Dichloromethane	3.0	298	0.3	—	—	0.49
1,4-Dioxane	2.3	298–318	0.38	—	—	—
	2.5	303	0.31	0.51	—	—
Methyl acetate	2.3	298-318	0.45	—	—	—
	2.5	303	—	0.43	0.59	—
Nitromethane	2.3	298-318	0.43	—	—	—
2-Picoline	2.3	298	0.36	—	—	—
3-Picoline	2.3	298	0.285	—	—	—
4-Picoline	2.3	298	0.26	—	—	—
Pyridine	2.3	298–318	0.28	—	—	—
	2.5	303	—	0.07	0.09	—
Tetrahydrofuran	2.5	286	0.442	—	—	—

Second virial coefficients A_2

Polymer	Solvent	Temp. (K)	M_w 10^{-3} (g mol^{-1})	$A_2 \times 10^4$ (mol cm^3 g^{-2})	Reference
Cellulose acetate	Acetone	RT	60–173	9.4–5.8	(19)
Cellulose diacetate	Acetone	285.3	94	4.1	(20)
(DS = 2.46)		298.6	—	3.8	
		311.0	—	3.6	
		363.2	—	3.5	
		323.5	—	3.4	
	Butanone	303	71	−0.5	(21)
		313	—	−0.25	
		323	—	0	
		333	—	0.25	
		313	92	−0.25	
		323	92	0	
		323	141	−0.21	

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Mark-Houwink parameters: K and a[22,23]

Solvent	DS	Temp. (K)	$M_w \times 10^{-4}$ (g mol^{-1})	$K \times 10^3$ (ml g^{-1})	a
Acetone	2.0	298	27	133	0.616
	2.25–2.38	303	2.6–15	16	0.82
	3.0	293	14	2.38	1.0
		298	18	8.97	0.90
		298	30	3.30	0.760
		298	39	14.9	0.82
		298	69	28.9	0.725
Acetone/methylene chloride	3.0	298	1.4–13	2.2	0.95
Acetone/water (80/20)	3.0	293	11	2.65	1.0
Chloroform	3.0	293	13	2.2	0.95
		298	69	45.4	0.649
		303	18	14.4	0.800
		303	18	4.5	0.9
o-Cresol	3.0	303	18	6.15	0.9
Dichloromethane	3.0	293	69	24.7	0.704
Dimethylacetamide	0.49	298	15	191	0.6
	1.75	298	14	95.8	0.65
	2.0	298	19	39.5	0.738
	3.0	298	69	26.4	0.750
Dimethyl sulfoxide	0.49	298	15	171	0.61
Ethanol/methylene chloride (20/80 by vol.)	3.0	298	30	13.9	0.834
Formaldehyde	0.49	298	15	20.9	0.60
Methylene chloride	3.0	298	DP = 150–560	1.45*	0.83
Tetrachloroethane	2.86	298	—	5.8	0.90
Tetrahydrofuran	2.0	298	30	51.3	0.688
Trifluoroacetic acid	2.0	298	19	52.7	0.696
	3.0	298	69	39.6	0.706
Water	0.49	298	15	20.9	0.60

*From $\eta = K(\mathrm{DP})^a$, DP = degree of polymerization.

Unit cell dimension of cellulose triacetate (CTA)

	Lattice	Monomers per unit cell	Chain per unit cell	Cell dimension (Å)			Space group	Density (g cm^{-3})	Reference
				a	*b*	*c*			
CTA I	Orthogonal	4	2	23.63	6.27	10.43	$P2_1$	1.239	(24)
	Orthorhombic	16	8	44.3	13.45	10.47	$P2_1$	1.228	(25)
CTA II	Orthorhombic	8	4	24.68	11.52	10.54	$P2_12_12_1$	1.278	(26)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Theta temperature Θ	K	DS = 2.46		
		Acetone	428	(27)
		Butanone	310	(27)
			323	(21)
		Cellulose triacetate, acetone	300	(28)
Characteristic ratio $\langle r^2 \rangle_0/nl^2$	–	Cellulose diacetate, 298 K, light scattering		(22)
		Acetone	26.3	
		THF	13.2	
Persistence length	Å	Acetone	55.6	(29)
		Trifluoroethanol	59.7	
Chain conformation	–	CTA I and II	2_1 helix	(25)
Glass transition temperature	K	Conflicting data	243–473	(30)
Melting point	K	CTA I, annealed at 250°C for 15–30 min, DSC, 20°C min^{-1}	580	(25)
		CTA II annealed at 250°C for 15–30 min, DSC, 20°C min^{-1}	582	(25)
		DS = 2.3–2.5	508–528	(24)
Heat capacity (of repeat unit)	kJ K^{-1} mol^{-1}	Sheet	0.36–0.60	(6)
		Molding	0.36–0.51	
Deflection temperature	K	1.82 MPa	321–364	(6)
		0.455 MPa	326–371	
Tensile modulus	MPa	Sheet	$(2.1–4.1) \times 10^3$	(6)
		Molding, lightly cross-linked	$(0.45–2.8) \times 10^3$	(6)
		$\overline{M}_c = 12{,}300$ g mol^{-1}	2,300	(31)
Tensile strength	MPa	Molding, lightly cross-linked	14–248	(6)
		$\overline{M}_c = 12{,}300$ g mol^{-1}	10	(31)
Maximum extensibility	%	Sheet	20–50	(6)
		Molding	60–70	
Compressive strength	MPa	Molding, ASTM D695	14–248	(6)
Flexural yield strength	MPa	Sheet	41–69	(6)
		Molding	14–110	
Impact strength	J m^{-1}	Molding, 0.5 by 0.5 in notched bar, Izod test, ASTM D256	21–278	(6)

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PROPERTY	UNITS	CONDITIONS			VALUE		REFERENCE
Hardness	R scale	Rockwell					
		Sheet			85–120		(6)
		Molding			34–125		
Index of refraction n	–	–			1.47–1.48		(32)
Refractive index increment dn/dc	ml g^{-1}	DS	Solvent	Temp. (K)	dn/dc (λ_0 nm)		
		0.49	DMA	–	0.068 (436)		(33)
		0.49	Formamide	–	0.069 (436)		(33)
		0.49	Water	–	0.131 (436)		(33)
		1.75	DMA	298	0.046 (436)		(33)
		2.45	THF	298	0.071 (436)		(33)
		2.45	Trifluoroethanol	298	0.157 (436)		(33)
		2.46	Acetone	298	0.122 (436)		(20, 21)
		2.46	Acetone	298	0.109 (546)		(20)
		3	DMA	298	0.040 (436)		(32)
Resistivity of cellulose acetate fiber	ohm cm^{-1}	RH (%)			Commercial	Purified	(32)
		45			967,000	81,500,500	
		55			424,000	6,040,000	
		65			150,000	448,000	
		75			28,900	33,200	
		85			1,610	2,460	
		95			11	39	
Permeability coefficient P	m^3 (STP) m s^{-1} m^{-2} Pa^{-1} ($\times 10^{17}$)	Permeant	Temp. (K)				
		H_2	293		2.63		(34)
					22.1–9.5		(35)
		He	293		10.2		(34)
		N_2^*	303		0.21		(34)
		O_2^*	303		0.585		(34)
		CO_2^*	303		17.3		(34)
					63.4–73.7		(35)
		H_2O	298		4130		(34)
		H_2O^*	298		5500		(34)
		H_2S	303		2.63		(34)
		H_2S^*	303		4.58		(34)
		$C_2H_4O^*$	303		30.0		(34)
		CH_3Br^*	303		4.2		(34)
Surface tension	mN m^{-1}	Contact angle			45.9		(36)
Thermal conductivity	W m^{-1} K^{-1}	293 K			0.20		(37)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Water absorption	%	25% RH	0.6	(1)
		50% RH	2.0	
		75% RH	3.8	
		95% RH	7.8	
Flammability	cm min^{-1}	—	1.27–5.08	(35)
Supplier	Eastman Chemical Co., P.O. Box 431, Kingsport, Tennessee 37662, USA			

*Film with plasticizer.

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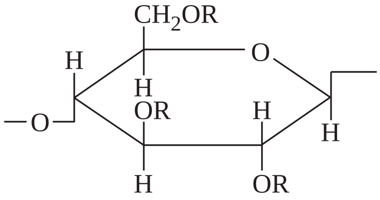
Cellulose butyrate

YONG YANG

ACRONYM CB

CLASS Carbohydrate polymers

STRUCTURE



(R is COC_3H_7 or H)

MAJOR APPLICATIONS Used as cellulose acetate butyrate in lacquers, coatings, hot-melt adhesives, and plastics.

PROPERTIES OF SPECIAL INTEREST Good tolerance for inexpensive lacquer solvents and common diluents.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight of (repeat unit)	$g\ mol^{-1}$	Degree of substitution (DS) = 3.0	372.41	–
Preparation	Cellulose + Butyric anhydride $\xrightarrow[-H_2O]{[H_2SO_4]/\Delta}$ Cellulose butyrate			(1)
Density	$g\ cm^{-3}$	–	1.17	(1)
IR (characteristic absorption frequencies)	cm^{-1}	Assignment		(2)
		(C_3H_7) stretching	2,960	
		(C_3H_7) stretching	2,940	
		(C_3H_7) stretching	2,870	
		(C=O) stretching	1,750	
		(C_3H_7) stretching	1,460	
		(C_3H_7) deformation	1,420	
		(C_3H_7) deformation	1,380	
		(C_3H_7) deformation	1,370	
		(C_3H_7) deformation	1,310	
		(C_3H_7) deformation	1,250	
		Structural factors	1,170	
		Structural factors	1,080	
Solubility parameter δ	$(MPa)^{1/2}$	–	17–24	(3)

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Cellulose butyrate

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Theta temperature Θ	K	Dodecane/tetralin (75:25 vol) Tetrachloroethane	395 329.7	(3) (4)
Solvents	–	For cellulose tributyrate	Benzene, chloroform, cyclohexanone, dodecane/tetralin (3:1, >130°C), tetrachloroethane, xylene (hot)	(4, 5)
Nonsolvents	–	For cellulose tributyrate	Cyclohexane, diethyl ether, 2-ethylhexanol, hexane, methanol	(4, 5)

Mark-Houwink parameters*: K and a[6]

Solvent	Method	Temp. (K)	$M_w \times 10^{-4}$ (g mol^{-1})	$K \times 10^3$ (ml g^{-1})	a
Butanone	Light scattering	303	6–32	4.3	0.87
	Osmometry	303	8-22	18.2	0.80
Tributyrin	Light scattering	273	6–32	5.3	0.87
	Light scattering	298	6–32	5.6	0.85
	Light scattering	323	6–32	6.1	0.82
	Light scattering	343	6–32	6.2	0.80
Dodecane/tetralin (75/25 by vol)	Osmometry	403	11–21	82	0.50

*For cellulose tributyrate.

Unit cell dimension of cellulose tributyrate[6,7]

Lattice	Monomers per unit cell	Chains per unit cell	Cell dimension (Å)		
			a	b	c
Orthorhombic	16	8	31.3	25.6	10.36

PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Degree of crystallinity of cellulose tributyrate	(%)	Annealing temp. (K)	Annealing hours		(8)
		298	18	36	
		363	136	40	
		373	72	39	
		383	18	41	
		393	18	43	
		403	18	43	
		413	18	45	
Chain conformation	–	–		2_1 helix	(9)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of fusion (of repeat unit)	kJ mol^{-1}	–	12.6	(9)
			12.8	(8)
Density (crystalline)	g cm^{-3}	–	1.192	(9)
Glass transition temperature	K	DS = 3.0	388	(10)
		DS = 3.0, 100% amorphous, DSC	354	(8)
Melting point	K	–	206–207	(9)
			354	(8)
Heat capacity (of repeat unit)	kJ mol^{-1}	–	0.108	(8)
Tensile strength	MPa	–	30.4	(1)
Water absorption	–	Relative humidity (%)		(1)
		25	0.1	
		50	0.2	
		75	0.7	
		95	1.0	

Refractive index increment *dn/dc* (ml g^{-1}), Reference (11):

Solvent	DS	Temp. (K)	*dn/dc* (λ_0 nm)
Bromoform	3.0	294	−0.11 (546)
Dimethylformamide	3.0	314	0.0442 (436)
			0.0478 (546)
Dioxane/water (93.5/6.5 vol)	3.0	336	0.104 (546)
Methyl ethyl ketone	3.0	294	0.078 (546)

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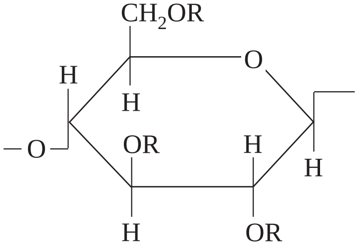
Cellulose nitrate

YONG YANG

ACRONYM CN

CLASS Carbohydrate polymers

STRUCTURE



(R is NO_2 or H)

MAJOR APPLICATIONS Protective and decorative lacquer coatings, rotogravure and flexographic inks, leather finishes, fabric and household adhesives, explosives, propellants, plastics.

PROPERTIES OF SPECIAL INTEREST Soluble in a wide variety of organic solvents, fast solvent release under ambient drying conditions, durability, toughness.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	Degree of substitution (DS) = 3.0	297.13	—
Preparation	Cellulose + HNO_3 → Cellulose nitrate			(1)
IR (characteristic absorption frequencies)	cm^{-1}	Assignment		(2, 3)
		(OH) stretching	3,450	
		(CH_2) stretching	2,970	
		(CH_2) stretching	2,940	
		(ONO_2) stretching	1,650	
		(ONO_2) stretching	1,280	
		(ONO_2) stretching	840	
		(C–C–O) stretching	1,070	
Thermal expansion coefficient	K^{-1}	—	$(8–12) \times 10^{-5}$	(4)
Specific gravity	$g\,cm^{-1}$	DS = 2.20–2.32	1.58–1.65	(1)
Solubility parameters δ	$(MPa)^{1/2}$	DS = 2.21	21.7	(5)
			30.39	(5)
			23.5	(5)
		DS = 2.08	21.93	(5)
		DS = 2.21	21.44	(6)

Solvents and nonsolvents[1,7,8]

DS	Solvent	Nonsolvent
1.00	Water	
1.83–2.32	Acetone*, acetic acid (glacial), lower alcohols, alcohol/diethyl ether, amyl acetate, *n*-butyl acetate*, butyl lactate, γ-butyrolactin*, cyclopentanone*, diethyl acetate*, diethyl ketone*, *N,N*-dimethylacetamide*, dimethyl carbonate*, dimethyl cyanamide*, dimethylformamide*, dimethyl maleate*, dimethylsulfoxide*, 2-ethoxyethyl acetate, ethyl acetate*, ethyl amyl ketone, ethylene glycol ethers, ethyl lactate, 2-hexanone*, methyl acetate*, methyl ethyl ketone*, methyl propyl ketone*, *n*-methylpyrrolidone-2*, 2-octanone*, 1-pentanone*, *n*-pentyl acetate*, pyridine*	Higher alcohols, higher carboxylic acids, higher ketones, tricresyl phosphate
2.48	Acetone*, cyclohexanone, ethanol/diethyl ether, ethyl butyrate, ethylene carbonate, ethylene glycol ether acetates, ethyl lactate, halogenated hydrocarbons, methyl acetate*, methyl amyl ketone*, furan derivatives, nitrobenzene	Alcohols, aliphatic hydrocarbons, aromatic hydrocarbons, carboxylic acids, dil, ethylene glycol, diethyl ether, water

*Forms liquid crystalline mesophase.

Polymer–liquid interaction parameters χ (ϕ_2) at various volume fractions of polymer ϕ_2[6,9,10]

Solvent	DS	Temp. (K)	$\chi(0)$	$\chi(0.2)$	$\chi(0.4)$	$\chi(0.6)$	$\chi(0.8)$	$\chi(1.0)$
Acetone	2.4	298	0.27	–	–	–	–	–
		303	0.24	0.05	–	–	–	–
	2.6	293	–	0.14	0.06	−0.37	−1.24	–
Acetonitrile	2.6	293	–	–	0.59	0.42	0.12	−0.1
Amyl acetate	2.4	298	0.02	–	–	–	–	–
2-Butanone	2.4	298	0.21	–	–	–	–	–
Butyl acetate	2.4	298	0.015	–	–	–	–	–
Cyclopentanone	2.6	293	–	0.42	0.07	−0.71	−2.4	–
2,4-Dimethyl-3-pentanone	2.6	293	−0.89	−1.8	−1.7	–	–	–
1,4-Dioxane	2.4	293	–	–	1.2	−0.25	−1.7	–
Ethyl acetate	2.4	298	0.02	–	–	–	–	–
	2.6	293	–	0.04	−0.43	−1.35	–	–
Ethyl formate	2.6	293	–	−0.08	−0.14	−0.42	−3.2	–
Ethyl *n*-propyl ether	2.6	293	–	–	–	1.20	–	–
2-Heptanone	2.4	298	0.02	–	–	–	–	–
2-Hexanone	2.4	298	0.15	–	–	–	–	–
Isopentyl acetate	2.6	293	–	−0.89	−1.8	−3.3	–	–
Isoproyl ketone	2.6	293	–	0.62	−0.08	−1.7	–	–
Methyl acetate	2.4	298	0.30	–	–	–	–	–
		303	0.17	−0.06	–	–	–	–
Methyl *t*-butyl ketone	2.6	293	–	0.016	−.5	−2.8	−3.7	–
Methyl isopropyl ketone	2.6	293	–	−0.5	−0.52	−1.6	–	–

Solvent	DS	Temp. (K)	$\chi(0)$	$\chi(0.2)$	$\chi(0.4)$	$\chi(0.6)$	$\chi(0.8)$	$\chi(1.0)$
Nitromethane	2.6	293	—	0.66	0.64	0.60	0.45	—
2-Octanone	2.4	298	0.16	—	—	—	—	—
Propyl acetate	2.4	298	0.13	—	—	—	—	—
	2.6	293	—	−0.38	−0.83	−2.0	−4.1	—

Second virial coefficients A_2

Conditions	Solvent	Temp. (K)	$M_w \times 10^{-3}$ (g mol^{-1})	Method	$A_2 \times 10^4$ (mol cm^3 g^{-2})	Reference
DS = 2.91	Acetone	298	81–3,850	Light scattering	10.8–8.2	(11)
DS = 2.55	Acetone	298	141–1,700	Light scattering	13.3–12.5	(11)
DS = 2.78	Acetone	RT	61.6–2,482	Osmometry	0.24	(11)
	—	298	77–2,640	Light scattering	6.10	(11)
	—	—	780	Light scattering	11.2	(11)
From raw cotton						
DS = 2.82	Acetone	288	22.8–417	Osmometry	0.24	(11)
DS = 2.87	Ethyl acetate	—	~1,000	Light scattering	6.2–7.0	(12)
From cotton	Acetone	293	31–661	Osmometry	0.28	(11)
	Butyl acetate	293	150–400	Light scattering	1.0−0.5	(11)
	—	298	30–360	Osmometry	3.5−0.3	(11)
From viscose rayon	Ethyl acetate	303	71.5	Osmometry	44.1	(11)
From chemical cotton	—	—	295–450	Osmometry	28.5–25.7	(11)
DS = 2.39	Butanone	298	130	Osmometry	10.8	(11)

Mark-Houwink parameters: K and a[13]

Polymer	Solvent	Temp. (K)	$M_w \times 10^{-4}$ (g mol^{-1})	$K \times 10^3$ (ml g^{-1})	a	Method
Cellulose	Acetone	293	250	2.80	1.00	Sedimentation
Trinitrate		298	265	1.69	1.00	Light scattering
		298	250	1.66	0.86	Light scattering
		298	32	10.8	0.89	Light scattering
(DS = 2.55)		298	200	5.70	0.90	Light scattering
(DS = 2.91)		298	400	6.93	0.91	Light scattering
		298	50	7.00	0.933	Osmometry
		298	100	11.0	0.91	Osmometry
		298	26	23.5	0.78	Osmometry
	Butyl acetate	298	50	5.68	0.969	Osmometry
	Butyl formate	298	26	23	0.81	Osmometry
	Cyclohexanone	298	22	2.24	0.810	Osmometry
	Ethyl acetate	298	100	3.8	1.03	Osmometry
		298	26	8.3	0.90	Osmometry
		298	250	1.66	0.86	Light scattering
		303	57	2.50	1.01	Light scattering
	Ethyl butyrate	298	50	3.64	1.0	Osmometry
	Ethyl formate	298	26	30	0.79	Osmometry

Polymer	Solvent	Temp. (K)	$M_w \times 10^{-4}$ (g mol^{-1})	$K \times 10^3$ (ml g^{-1})	a	Method
	Ethyl lactate	298	65	12.2	0.92	Osmometry
	2-Heptanone	298	26	5.0	0.93	Osmometry
	Methyl acetate	298	22	18.3	0.835	Osmometry
	Nitrobenzene	298	22	6.1	0.945	Osmometry
	Pentyl acetate	298	26	1.1	1.04	Osmometry

Persistence length

Conditions	Solvent	Temp. (K)	Persistence length (nm)	Reference
DS = 2.91	Acetone	298	970	(13)
DS = 2.55	Acetone	298	530	(13)
DS = 2.75	Ethyl acetate	303	700	(13)
DS = 2.26	Acetone	293	0.48	(13)
Cellulose trinitrate	Acetone	298	360	(13)
		295	0.26 ± 0.01	(13)
		293	0.40–0.70	(13)
Cellulose trinitrate	Acetone	—	13.2	(14)
	Ethyl acetate	—	11.8	(14)

Unit cell dimension of cellulose trinitrate

Lattice	Monomers per unit cell	Cell dimension (Å)			γ	T_m (K)	Heat of fusion (kJ mol^{-1})	Chain conformation	Reference
		a	*b*	*c*					
Orthorhombic	10	12.25	25.4	9.0	—	697	3.8	51	(15, 16)
Orthorhombic	10	9.0	14.6	25.4	—	700	6.3	52	(16)
Monoclinic (CTNII)	10	12.3	8.55	25.4	91°	—	—	—	(17)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Huggins constants: k' and k''	—	—	—	(11)
Glass transition temperature	K	—	326, 329	(18)
Heat capacity	kJ K^{-1} mol^{-1}	—	0.37–0.50	(4)
Deflection temperature	K	At 1,820 KPa	60–71	(4)
Tensile modulus	MPa	—	1,310–1,520	(4, 19)
Tensile strength	MPa	RS, 296 K, 50% RH	62–110 48.3–55.2	(1) (19)
Maximum extensibility	%	RS, 296 K, 50% RH	13–14 40–45	(1) (4)

PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Compressive strength	MPa	ASTM D695			152–241	(4)
Flexural yield strength	MPa	–			62–75.9	(4)
Impact strength	$J\,m^{-1}$	0.5 by 0.5 in notched bar , Izod test, ASTM D256			267–374	(4)
Hardness	–	RS, Sward, % on glass			90	(1)
		Rockwell, R scale			95–115	(4)
Index of refraction n	–	–			1.51	(1)
Refractive index increment dn/dc	$ml\,g^{-1}$	Solvent	DS	Temp. (K)	dn/dc (λ_0 nm)	(12, 20)
		Acetone	1.96	298	0.1022 (436), 0.0998 (546)	
			2.23	–	0.1010 (436), 0.0985 (546)	
			2.26–2.35	293	0.107 (436), 0.0950 (546)	
			2.43	298	0.0968 (436)	
			2.55	–	0.1151 (436)	
			3.0	298	0.0930 (436), 0.0903 (546), 0.098 (1086)	
		Ethyl acetate	2.05	293	0.103 (546)	
			2.77	298	0.102 (436)	
			–	293	0.107 (436)	
			2.87	–	0.105 (436, 546)	
			3.0	303	0.102 (436)	
			–	298	0.107 (436)	
			–	293	0.105 (436), 0.103–0.105 (546)	
Dielectric constant ε''	–	293–298 K				(1)
		60 Hz			7–7.5	
		1,000 Hz			7	
		1×10^6 Hz			6	
Power factor	%	293–298 K				(1)
		60 Hz			3–5	
		1,000 Hz			3–6	
Surface tension	mNm^{-1}	–			38	(21)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	–			0.23	(22)
Water absorption	%	294 K, 24 h, 80% RH			1.0	(1)

PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Compatible polymers	Cellulose acetate, ethyl cellulose, ethylhydroxyethylcellulose, poly(carprolacton), poly(vinyl acetate)				(19, 23)
Permeability coefficient *P*	m^3(STP) m s^{-1} m^{-2} Pa^{-1} ($\times 10^{17}$)	Permeant	Temp. (K)		(24)
		H_2	293	1.5	
		He	298	5.18	
		N_2	298	0.087	
		O_2	298	1.46	
		Ar	298	0.0825	
		CO_2	298	1.59	
		NH_3	298	42.8	
		H_2O	298	4,720	
		SO_2	298	1.32	
		C_2H_6	298	0.0473	
		CH_3H_8	298	0.0063	
Cost	US$ kg^{-1}	In 30% isopropanol		3.7–5.5	–
Supplier	Hercules Inc., 1313 North Market Street, Wilmington, DE 19894, USA				

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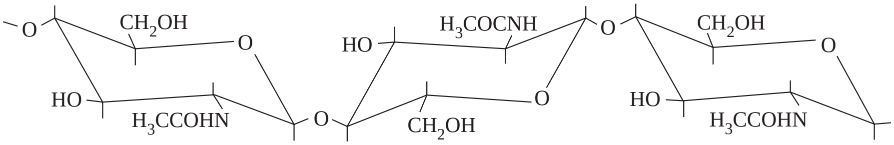
Chitin

RACHEL MANSENCAL

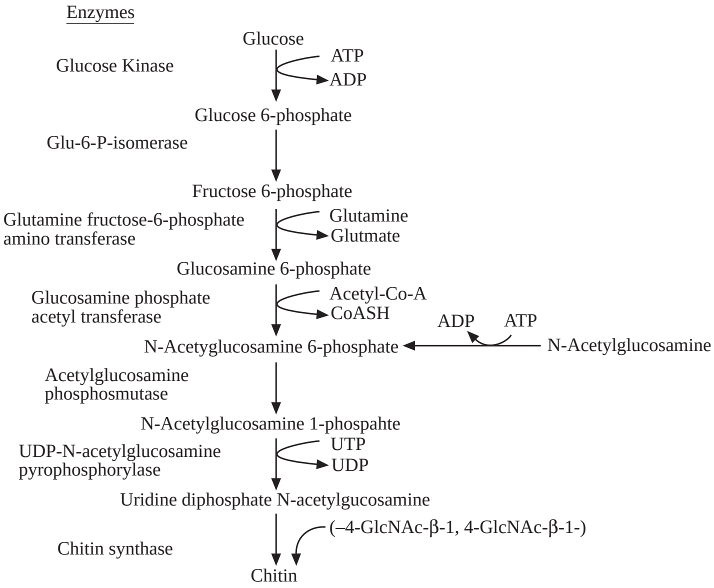
CLASS Carbohydrate polymers; polysaccharides

STRUCTURE



NATURAL RESOURCES Chitin is a biopolymer found in crustaceans shells (crab, shrimp, prawn, lobster) in some mollusks (krill, oyster, clam shells, squid skeleton). It is also found in fungi (mushrooms, yeast) and in various insects (cockroaches, silkworms, spiders, beetles).[1–2]

BIOSYNTHESIS[1–2]



EXTRACTION Chitin is produced by removing calcium carbonate and proteins from the shells.[1]

MAJOR APPLICATIONS Biomedical (wound and burn healing, treatment of fungal infections, antitumor agent, hemostatic agent, etc.); cosmetics (additives); biotechnology (enzyme and cell immobilization); industry (paper industry, food industry, etc.); agriculture and environmental protection.[1–3]

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PROPERTIES OF SPECIAL INTEREST Natural resources; basic polysaccharides; nontoxic; biodegradability; bioactivity; biosynthesis; interesting derivatives (chitosan); toughness; graft copolymerization; chelating ability for transition metal cations; immobilizes enzymes by chemical linking or adsorption; chiral polymer.[1–4]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Infrared absorption (wavelength)	cm^{-1}	α-chitin	3,450; 3,265; 3,102; 2,950; 2,922; 2,887; 1,654; 1,548; 1,414; 1,377; 1,310; 1,261; 1,205; 1,115; 1,072; 1,026; 953; 893	(5, 6)
		β-chitin	3,295; 1,430; 972; 638	
^{13}C NMR (chemical shift)	ppm	C=O	173.7	(7–9)
		C_1	103.7	
		C_4	83.7	
		C_5	75.6	
		C_3	73.2	
		C_6	60.6	
		C_2	55.2	
		CH_3	22.6	
X-ray diffraction peaks	Degrees	–	8°58′–10°26′ 19°58′–20°00′	(10)
Molecular weight	$g\,mol^{-1}$	Native chitin	$>10^6$	(1–4)
		Commercial chitin	$(1–5) \times 10^5$	
Moisture	%	–	2–10	–
Nitrogen content	%	–	6–7	–
Deacetylation	%	–	10–15	–
Dissociation constant K_a	–	–	6.0–7.0	–
Ash	%	900°C	<1.0	–
Transition metals	$\mu g\,g^{-1}$	–	<5.0	(1–4)
Solubility	–	Nonsoluble in classical solvent	–	(4)
	–	Soluble in N-N dimethyl-acetamide and 5% LiCl	Up to 5%	
Protein content	%	Amino-acid catalyst	<0.5	(4)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Biodegradability (effective microorganisms)	Chitinoclastic bacteria Chitinase associated with chitobiases, β-N, acetylhexosaminidases, and lysozymes	Normal pH = 4.0–7.0	Very slow Most active	(2)
Toxicity	$g\,kg^{-1}$ body weight	LD 50	16	(1)

Unit cell dimensions[(10–13)]

Isomer	Monomers per unit cell	Lattice	Space group	Cell dimensions (Å)			Cell angle (°)
				a	*b*	*c* (fiber axis)	γ
α-chitin	2 (antiparallel arrangement of the chains)	Orthorhombic	$P2_12_12_1$	4.74	1.88	1.032	90
β-chitin	2 (parallel arrangement of the chains)	Monoclinic	$P2_2$	4.85	9.26	10.38	97.5

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Collagen

CHANDIMA KUMUDINIE AND JAGATH K. PREMACHANDRA

CLASS Polypeptides and proteins

STRUCTURE The most common type of collagen, Collagen I, is composed of two kinds of polypeptide helices, $\alpha 1$ and $\alpha 2$, in a 2:1 ratio respectively, to form a triple helix. The $\alpha 1$ and $\alpha 2$ chains of tropocollagen have a regularly repeating sequence of amino acid residues in which glycine is found at every third residue. This sequence can be written $(\text{GLY-X-Y})_n$, where X and Y are often proline and hydroxyproline respectively.[1]

FUNCTIONS An extracellular protein, which is responsible for the strength and flexibility of connective tissue. Accounts for 25–30% of the protein in an animal.[2] Major component in all mammalian tissues including skin, bone cartilage, tendons, and ligaments.[3]

MAJOR APPLICATIONS Biomaterial applications such as dermal implant, carrier of drugs, cell culture matrix, wound dressing, material for hybrid organ, drug delivery system, soft contact lens, tissue implants, cardiovascular graft, artificial heart, etc. Synthetic sausage casings in food industry.[3,4]

Major types of collagen[1,5]

Molecular formula	Composition	Tissue distribution
$(\alpha 1)_2\ \alpha 2$ Type I chains	Low hydroxylysine, low carbohydrate, broad fibrils	Tendons, bone, skin, ligaments, cornea, internal organs (comprises 90% of body collagen)
$(\alpha 1)_3$ Type II chains	High carbohydrate, high hydroxylysine, thin fibrils	Cartilage, vitreous body of eye, intervertebral disc
$(\alpha 1)_3$ Type III chains	Low carbohydrate, high hydroxylysine, high hydroxyproline	Blood vessels, skin, internal organs
$(\alpha 1)_3$ Type IV chains	High hydroxylysine, high carbohydrate	Basal laminae
$(\alpha 1)_2\ \alpha 2$ Type V chains	High carbohydrate, high hydroxylysine	Many tissues in small amounts

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Biosynthesis of collagen[6]

Step 1. Translation on ribosome

↓

Step 2. Hydroxylation of Pro and Lys

↓

Step 3. Release from ribosome and addition of sugars

↓

Step 4. Formation of triple helix and folding of globular domains

↓

Step 5. Secretion from cell

↓

Step 6. Removal of N and C terminal domains

↓

Step 7. Deamination of lysine residues to form aldehyde and formation of cross-links

Selected amino acid analysis of collagens[7]

Amino acid*	Collagen					
	α (I)[a]	α 2[a]	α 2[b]	α (II)[c]	α (III)[a]	α (IV)[d]
3-Hydroxyproline	1	0	1	2	0	11
4-Hydroxyproline	96	82	86	99	125	130
Aspartic acid	41	47	49	42	42	51
Threonine	16	19	19	20	13	23
Serine	37	35	37	26	39	37
Glutamic acid	71	68	73	90	71	84
Proline	133	120	107	121	107	61
Glycine	336	337	324	332	350	310
Alanine	115	105	102	100	96	33
Cysteine	0	0	0	0	2	8.0
Valine	20	33	37	18	14	29
Methionine	7	5	4.6	9	8	10
Isoleucine	7	15	17	9	13	30
Leucine	20	30	34	25	22	54
Tyrosine	1.9	4.6	3.0	1	3	6
Phenylalamine	12	12	12	13	8	27
Hydroxylysine	5.4	7.6	11.5	14	5	44.6
Lysine	30	22	21	22	30	10
Histidine	2	10	7.9	2	6	10
Arginine	49	51	53	51	46	33
Galactose	—	—	1.0	—	—	34.0
Glucose	—	—	0.65	—	—	2.0

*Values expressed as residues per 1,000 amino acids.
[a]Human skin. [b]Human cornea. [c]Human cartilage. [d]Human glumerular basement membrane.

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Typical molecular weight range of polymer M_w	g mol^{-1} ($\times 10^5$)	Calf skin, solvents: citrate pH 3.7, phosphate pH 7.4, sedimentation equilibrium	2.5–3.1	(8)
		Calf skin, solvent: citrate pH 3.7, viscosity	3.5	(8)
		Dogfish shark skin, solvent: formate pH 3.8, sedimentation equilibrium	<3.5	(8)
		Chick cartilage and skin, sedimentation equilibrium	2.62–3.07	(9)
		Type I collagen, rat tail tendon, aggregates in 0.01 M HCl	8.05	(10)
		Type I collagen, single molecules	2.82	(10)
IR (characteristic absorption frequencies)	cm^{-1}	N–H stretch	3,330	(11)

CHAIN CONFORMATION	REFERENCE
Collagen I, the most common type of collagen, is composed of two kinds of polypeptide helices, $\alpha 1$ and $\alpha 2$, in a 2:1 ratio respectively, to form a triple helix. The $\alpha 1$ and $\alpha 2$ chains of tropocollagen have a regularly repeating sequence of amino acid residues in which glycine is found at every third residue. This sequence can be written (GLY-X-Y)$_n$, where X and Y are often proline and hydroxyproline.	(1)
Arranged in fibrils, composed of microfibrils, characteristic striation with a repeat distance of about 670 Å.	(2)
Consists of macrofibrils, fibrils, and subfibrils of diameters ~10^4 Å, 10^3 Å, and 10^2 Å respectively, spun collagen fiber after thermal treatment at 170°C, by scanning electron microscopy.	(12)
Helical structure, when heated above 40°C, the helices loosen and form thread-like chains and the collagen becomes gelatin.	(3)
Triple helix, by optical rotatory dispersion.	(4)
Rodlike with a length ~2,800 Å, by light scattering.	(11)
Helical rod, length ~3,000 Å and width ~15 Å.	(13)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Linear thermal expansion coefficient	K^{-1}	Whale ligament	~0	(14)
		Rat tail tendons	3.24×10^{-4}	
Density	g cm^{-3}	At 25°C, in 8 M LiBr-diethyleneglycol monobutyl ether		(14)
		Rat tail tendon from a 2-month-old rat	1.30	
		Rat tail tendon from a 10-month-old rat	1.30	
		Whale ligament	1.32	
		Rat tail tendon cross-linked with 1,3-bis(vinylsulfonyl)-2-propanol (BVSP)	1.33	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	g cm^{-3}	At 25°C, in 8 M LiBr-diethyleneglycol nonomethyl ether, cross-linked with BVSP, rat tail tendon	1.34	(14)
Solubility	Collagen in its mature form is insoluble under physiological conditions, can be denatured by heat, mild acid, or alkaline treatment			(2)
Second virial coefficient	mol cm^3 g^{-2}	Solvent: 2 M KCNS at 25°C	3.0×10^{-4}	(11)
Degree of crystallinity	%	X-ray diffraction from collagen fibers	20–40	(11)
Denaturation temperature	K	Non-cross-linked, spun collagen fibers		(12)
		Before thermal treatment	316	
		100°C for 30 min	314	
		170°C for 30 min	312	
		3 wt% glutaraldehyde cross-linked		(12)
		Before thermal treatment	337	
		100°C for 30 min	337	
		170°C for 30 min	318	
		7 wt% Cr-tanned		(12)
		Before thermal treatment	365	
		100°C for 30 min	360	
		170°C for 30 min	353	
		Type I collagen	312.6	(15)
		Type II collagen	314.0	(15)
		Type III collagen	312.2	(15)
		In 0.1 M acetic acid by optical rotation		(9)
		Chick cartilage	313.7	
		Chick skin	315.5	
		Lamb anterior lens capsule by circular dichroism spectroscopy	313	(16)
		Pig kidney collagen	310	(17)
		Muscle layer collagen in Ascaris	313	(17)
		Intact collagen		(18)
		Bovine semimembranosus	343.6	
		Bovine longissimus dorsi	344.3	
		Bovine longissimus dorsi, after 1-week storage	340.2	
		Bovine longissimus dorsi	344.5	
		Rat skin	341.3	
		Bovine tendon	340.7	
		Cod skin	323.6	
		Tropocollagen		(18)
		Calf skin	323.6	
		Rat skin	329.2	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Denaturation temperature	K	Type IV procollagen, optical rotatory dispersion, at neutral pH		(19)
		Heating rate $\sim 0.17^\circ C\,min^{-1}$	308–315, 321	
		Heating rate $\sim 0.027^\circ C\,min^{-1}$	307–314, 320	
		At neutral pH, DSC	309.0, 315.1, 321.0	
		In 10 mM acetic acid	308.6, 311.9, 314.7, 323.0	
		Soluble collagen, conc = $0.86\,mg\,ml^{-1}$, in 0.15 M potassium acetate buffer, pH 4.7, solvent:		(20)
		Ethylene glycol (1 M)	312.3	
		2-Methoxyethanol (1 M)	312.0	
		Control	311.9	
		2-Ethoxyethanol (1 M)	311.1	
		2-Butoxyethanol	308.3	
		Type IV collagen, bovine anterior lens capsules	327.4, 361.8	(21)
Transition enthalpy	$kJ\,mol^{-1}$	In 50 mM sodium citrate buffer, pH 3.9, in $kJ\,mol^{-1}$ in tripeptide units		(15)
		Type I collagen	17.0	
		Type II collagen	17.5	
		Type III collagen	16.5	
Heat capacity	$kJ\,K^{-1}\,mol^{-1}$	Native hydrated	1.60×10^{-3}	(22)
		Native anhydrous	1.22×10^{-3}	
Tensile modulus	MPa	Gauge length 2.0 cm, strain rate 50% min^{-1}		(23)
		Uncross-linked, unstretched fiber, wet diameter $d = 327\,\mu m$	1.8 ± 0.3	
		10% stretched fiber, uncross-linked, $d = 253\,\mu m$	5.7 ± 2.5	
		30% stretched fiber, uncross-linked, $d = 173\,\mu m$	20.8 ± 4.34	
		50% stretched fiber, uncross-linked, $d = 147\,\mu m$	46.0 ± 19.9	
		Unstretched fiber, cross-linked, $d = 94\,\mu m$	383 ± 112	
		10% stretched fiber, cross-linked, $d = 95.6\,\mu m$	429 ± 111	
		30% stretched fiber, cross-linked, $d = 86.1\,\mu m$	726 ± 120	
		50% stretched fiber, cross-linked, $d = 80.3\,\mu m$	766 ± 111	
		Gauge length = 1 cm, elongation rate = 100 mm min^{-1}		(24)
		Collagen-poly(lactic acid) (PLA) composites, 50% collagen fiber and 50% PLA matrix (w/w)	~37	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile modulus	MPa	Collagen-collagen composites, 50% collagen fiber and 50% collagen matrix (w/w)	~18	(24)
		Uncross-linked collagen matrix	10	(24, 25)
Shear modulus	MPa	At 25°C, in 8 M LiBr-diethyleneglycol monobutyl ether,		(14)
		Rat tail tendon from a 2-month-old rat	2.91×10^{-3}	
		Rat tail tendon from a 10-month-old rat	0.129	
		Whale ligament	0.172	
		Rat tail tendon cross-linked with 1,3-bis(vinylsulfonyl)-2-propanol (BVSP)	0.622	
		At 25°C, in 8 M LiBr-diethyleneglycol nonomethyl ether, rat tail tendon cross-linked with BVSP	0.602	(14)
Tensile strength	MPa	Gauge length 2.0 cm, strain rate 50% min^{-1}		(23)
		Uncross-linked, unstretched fiber, wet diameter $d = 327 \mu m$	0.91 ± 0.21	
		10% stretched fiber, uncross-linked, $d = 253 \mu m$	2.0 ± 1.2	
		30% stretched fiber, uncross-linked, $d = 173 \mu m$	5.9 ± 1.3	
		50% stretched fiber, uncross-linked, $d = 147 \mu m$	7.2 ± 1.3	
		Unstretched fiber, cross-linked, $d = 94 \mu m$	46.8 ± 17.1	
		10% stretched fiber, cross-linked, $d = 95.6 \mu m$	51.6 ± 17.0	
		30% stretched fiber, cross-linked, $d = 86.1 \mu m$	71.5 ± 18.3	
		50% stretched fiber, cross-linked, $d = 80.3 \mu m$	68.8 ± 15.8	
		Gauge length = 1 cm, elongation rate = 100 mm min^{-1}		(24)
		Collagen-poly(lactic acid) (PLA) composites, 50% collagen fiber and 50% PLA matrix (w/w)	~13	
		Collagen-collagen composites, 50% collagen fiber and 50% collagen matrix (w/w)	~7	(24)
		Uncross-linked collagen matrix	5	(24, 25)
		Gauge length = 2 cm, strain rate 1 mm min^{-1}		(12, 26)
		Uncross-linked fiber	~350	
		0.1 wt% glutaraldehyde (GA) cross-linked fiber	~300	
		1 wt% GA cross-linked fiber	~320	
		0.7 wt% Cr-tanned fiber	~425	
		7 wt% Cr-tanned fiber	~400	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Ultimate elongation	%	Gauge length = 2.0 cm, strain rate 50% min^{-1}		(23)
		Uncross-linked, unstretched fiber, wet diameter $d = 327\,\mu m$	68.0 ± 6.87	
		10% stretched fiber, uncross-linked, $d = 253\,\mu m$	45.1 ± 8.97	
		30% stretched fiber, uncross-linked, $d = 173\,\mu m$	32.5 ± 4.76	
		50% stretched fiber, uncross-linked, $d = 147\,\mu m$	24.1 ± 5.67	
		Unstretched fiber, cross-linked, $d = 94\,\mu m$	15.6 ± 2.66	
		10% stretched fiber, cross-linked, $d = 95.6\,\mu m$	15.5 ± 2.61	
		30% stretched fiber, cross-linked, $d = 86.1\,\mu m$	12.3 ± 1.75	
		50% stretched fiber, cross-linked, $d = 80.3\,\mu m$	11.6 ± 2.49	
		Gauge length = 1 cm, elongation rate = 100 mm min^{-1}		(24)
		Collagen-poly(lactic acid) (PLA) composites, 50% collagen fiber and 50% PLA matrix (w/w)	~20	
		Collagen-collagen composites, 50% collagen fiber and 50% collagen matrix (w/w)	~24	
		Gauge length = 2 cm, strain rate 1 mm min^{-1}		(12, 26)
		Uncross-linked fiber	~20	
		0.1 wt% glutaraldehyde (GA) cross-linked fiber	~30	
		1 wt% GA cross-linked fiber	~24	
		0.7 wt% Cr-tanned fiber	~22	
		7 wt% Cr-tanned fiber	~18	
Optical rotation	Degrees	At 589 μm		(17)
		Muscle layer collagen in Ascaris	−400	
		Pig kidney collagen	−380	
		Ascaris muscle layer, denatured	−150	
		Pig kidney, denatured	−130	
			−380 to −420	(13)
Electrical conductivity σ	S cm^{-1}	From bovine corium, dissolved in 1 mM HCl, conc. 0.19% at 5°C, temp. range ~20–50°C, heating rate = 0.3°C min^{-1}	~(1.5–2.25) $\times 10^{-4}$*	(27)
		Pepsin-solubilized prepared collagen, conc. 0.20% in 1 mM HCl, temp. range ~20–50°C, heating rate = 0.3°C min^{-1}	~(1.75–2.5) $\times 10^{-4}$	(27)
Permeability	cm S^{-1}	Collagen/poly(vinyl alcohol) (PVA) cross-linked films to NaCl at 37°C		(28)
		At 0 wt% PVA content	~5.5	
		At 50 wt% PVA content	~15	
		At 80 wt% PVA content	~17.5	
Translational diffusion coefficient	$cm^2\,S^{-1}$	Type I collagen rat tail tendon, aggregates in 0.01 M HCl	4.5×10^{-8}	(10)
		Type I collagen, single molecules	7.8×10^{-8}	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Intrinsic viscosity	$dl\ g^{-1}$	Ascaris muscle layer, in 0.5 M NaCl at 25°C	16	(17)
		Pig kidney, in 0.15 M sodium acetate, pH = 4.0, at ~25°C	12	
Average hydrophobicity	—	In chicken tendon	880	(29)
		α-fraction in calf skin	880	
		Spongin B in sponge	760	
		Sturgeon swim bladder	770	

*σ increased with temperature then decreased stepwise at ~40°C, and then increase again.

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Elastic, plastic, and hydrogel-forming protein-based polymers

CHI-HAO LUAN AND DAN W. URRY

CLASS Polypeptides and proteins

REPRESENTATIVE STRUCTURES

Elastomer	Poly(GβGαP)
Plastic	Poly(AVGVP)
Hydrogel	Poly(GGAP)

MAJOR APPLICATIONS *Medical*: soft tissue augmentation; cell attachment to elastic matrices; prevention of post-surgical adhesions; tissue reconstruction; coatings on catheters, leads, and tubings; drug delivery; biosensors. *Nonmedical*: controlled release of herbicides, pesticides, fertilizers, and growth factors; food product additives; material coating; transducers (sensors/actuators); molecular machines; biodegradable plastics; controllable super absorbents.[1]

PROPERTIES OF SPECIAL INTEREST Water soluble below a critical temperature. Hydrophobic folding and assembly (inverse temperature transition). Biocompatible. Biodegradable (chemical clocks enabling proteolytic degradation). Relatively low cost when microbially produced. To perform free energy transduction involving the intensive variables of mechanical force, temperature, pressure, chemical potential, electrochemical potential, and light. Thermoplastics (regular and inverse).[2,3]

SYNTHESIS Chemical synthesis using solution and solid phase methods. Microbial synthesis using gene construction and expression in the cells of animals and plants.

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Table 1. Hydrophobicity scale for protein-based polymers and proteins based on the properties of the inverse temperature transition of elastic protein-based polymers, poly[f_V(GVGVP), f_X(GXGVP)].[a]

Residue X: Three-letter abbreviation	Residue X: One-letter symbol	T_t (°C) (in pbs)[2]	T_b (°C) (in H_2O)[4,5]	$\Delta H^{(4,5)}$ (kcal mol^{-1})[b] ±0.05	$\Delta S^{(4,5)}$ (cal mol^{-1} K^{-1})[b] ±0.05
Lys (dihydro NMeN)[c]	–	−130	–	–	–
Trp	(W)	−90	−105	2.10	7.37
Tyr	(Y)	−55	−75	1.87	6.32
Phe	(F)	−30	−45	1.93	6.61
His (imidazole)	(H^O)	−10	–	–	–
Leu	(L)	5	5	1.51	5.03
Ile	(I)	10	10	1.43	4.60
Lys (6-OH tetrahydro NMeN)[c]	–	15	–	–	–
Met	(M)	20	15	1.00	3.29

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Residue X		T_t (°C) (in pbs)[2]	T_b (°C) (in H_2O)[4,5]	$\Delta H^{(4,5)}$ (kcal mol^{-1})[b] ±0.05	$\Delta S^{(4,5)}$ (cal mol^{-1} K^{-1})[b] ±0.05
Three-letter abbreviation	One-letter symbol				
Val	(V)	24	26	1.20	3.90
Glu($COOCH_3$)	(E^m)	25	—	—	—
Glu(COOH)	(E^O)	30	20	0.96	3.14
Cys	(C)	30	—	—	—
His (imidazolium)	(H^+)	30	—	—	—
Lys(NH_2)	(K^O)	35	40	0.71	2.26
Pro	(P)	−8[d], 40[e]	40[e]	0.92	2.98
Asp(COOH)	(D^O)	45	40	0.78	2.57
Ala	(A)	45	50	0.85	2.64
HyP	—	50	—	—	—
Thr	(T)	50	60	0.82	2.60
Asn	(N)	50	50	0.71	2.29
Ser	(S)	50	60	0.59	1.86
Gly	(G)	55	55	0.70	2.25
Arg	(R)	60	—	—	—
Gln	(Q)	60	70	0.55	1.76
Tyr(ϕ-O^-)	(Y^-)	120	140	0.31	0.94
Lys(NH_3^+)	(K^+)	120	—	—	—
Lys(NMeN,oxidized)[c]	—	120	—	—	—
Asp(COO^-)	(D^-)	170	—	—	—
Glu(COO^-)	(E^-)	250	—	—	—
Ser($PO_4^=$)	—	1,000	—	—	—

[a] T_t and T_b are the on-set temperature for the hydrophobic folding and assembly transition, that is, inverse temperature transition, in pbs (0.15 N NaCl, 0.01 M phosphate) as determined by light scattering and in water as determined by DSC, respectively. Both values are linearly extrapolated to $f_X = 1$ and rounded to a number divisible by 5. ΔH and ΔS are the values at $f_X = 0.2$ on the curve for a linear fit of the DSC derived endothermic heats and entropies of the transitions for the polymers in water.

[b] Per mole of pentamer.

[c] NMeN is for N-methyl nicotinamide pendant on a lysyl side chain, that is, N-methyl-nicotinate attached by amide linkage to the εNH_2 of Lys. N-methyl-1,6-dihydronicotinamide (dihydro NMeN) is the most hydrophobic reduced state, and the second reduced state is N-methyl-6-OH, 1,4,5,6-tetrahydronicotinamide (6-OH tetrahydro NMeN).

[d] The calculated T_t value for Pro comes from poly(GVGVP) when the experimental values of Val and Gly are used. This hydrophobicity value of −8°C is unique to the β-spiral structure where there is hydrophobic contact between the Val_i^1 γCH_3 and the adjacent Pro_i^2 δCH_2 and the interturn Pro_{i+3}^3 βCH_2 moieties.

[e] The experimental value determined from poly[f_V(GVGVP), f_P(GVGPP)].

Table 2a. Hydrophobic-induced pK shifts on polytricosamers and polymers of random mixtures of composite pentamers.*[6]

Glu-containing polymer	pKa
Poly[0.8(GVGVP), 0.2(GEGVP)]	4.3
Poly[GEGFP GVGVP GVGVP GVGVP GFGFP GFGFP]	7.7
Poly[(GEGFP), 3(GVGVP), 2(GFGFP)]†	4.7
Poly[GEGVP GFGFP GFGVP GVGVP GFGFP GVGVP]	7.8
Poly[GEGFP GVGVP GVGFP GFGFP GVGVP GVGFP]	8.1
Poly[(GEGFP), 2(GVGVP), 2(GVGFP), (GFGFP)]†	5.2

Asp-containing polymer	pKa
Poly[GDGFP GVGVP GVGFP GFGFP GVGVP GVGFP]	10.1
Poly[(GDGFP), 2(GVGVP), 2(GVGFP), (GFGFP)]†	4.6
Poly[GDGFP GVGVP GVGVP GVGVP GFGFP GFGFP]	9.5
Poly[(GDGFP), 3(GVGVP), 2(GFGFP)]†	5.2
Poly[GDGVP GFGFP GFGVP GVGVP GFGFP GVGVP]	6.7

* Experimental conditions: 40 mg ml^{-1} at 20°C, M.W. of the polypeptides > 50 kDa.
† Random mixture of pentamers comprising associated polytricosapeptide.

Table 2b. Hydrophobic-induced pK shift for poly[f_V(GVGIP), f_X(GXGIP)], where X = E, D, and K, and f_X varies from 0.06 to 1.0.[7,8,9]

f_E	0.06	0.15	0.31	0.37	0.42	0.49	0.70	0.77	0.90	1.00
pK*	6.08	5.70	4.90	4.70	4.55	4.50	4.40	4.35	4.35	4.35
pK†	6.61	5.92	5.03	4.80	4.48	4.40	4.35	4.40	4.55	4.70
f_D	0.06	0.08	0.19	0.28	0.35	0.51	0.73	0.84	0.89	1.00
pK*	5.4	5.2	4.7	4.3	4.1	4.0	3.9	3.9	3.9	3.8
pK†	6.0	5.0	4.5	4.2	3.9	3.8	3.9	4.1	4.2	4.6
f_K	0.06	0.09	0.14	0.22	0.41	0.59	0.76	0.88	0.91	1.00
pK*	8.60	8.90	9.13	9.38	9.59	9.68	9.70	9.65	9.60	9.40
pK†	8.18	8.65	8.85	9.11	9.43	9.55	9.60	9.62	9.58	9.20

* In 0.15 N NaCl; †In H_2O; M.W. of the polypeptides > 50 kDa; at 37°C.

Table 2c. Stretch-induced pK shifts for cross-linked Glu-containing polymers.

Polymer	ΔpK	Force		pK
		dynes cm^{-2}	grams	
X20-poly[0.8(GVGVP), 0.2(GEGVP)]*[10]	0.0	0.0	0.0	3.99
	0.85	—	1.0	4.84
X20-poly[0.82(GVGIP), 0.18(GEGIP)]*[11]	0.0	0.0	0.0	6.2
	0.37	3.6×10^5	1.0	6.57
	0.65	5.4×10^5	1.5	6.85
	1.25	6.4×10^5	1.75	7.45
	1.95	7.3×10^5	2.0	8.15
	2.8	8.0×10^5	2.2	9.0

* X20 indicates 20 Mrad γ-irradiation cross-linked polymer matrix.

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Table 3a. Composition effect on inverse temperature transition in water.*[3,5]

Polymer	T_b (°C)	T_m (°C)	ΔQ (cal g^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} K^{-1})
Poly(AVGIP)	18.4	19.7	10.39	4.54	15.46
Poly(AVGVP)	33.6	34.7	6.20	2.62	8.47
Poly(GVGIP)	11.2	13.3	6.31	2.67	9.32
Poly(GVGVP)	27.8	30.0	2.69	1.10	3.59
$(GVGVP)_{251}$	26.9	29.0	3.21	1.32	4.31
Poly[(GVGVP), (GVGIP)]	18.9	20.3	4.24	1.77	5.98
Poly[0.8(GVGVP), 0.2(GFGVP)]	12.9	16.0	4.58	1.92	6.54
Poly[0.8(GVGVP), 0.2(GAGVP)]	31.8	34.9	1.99	0.80	2.57
Poly(GVGVAP) (irreversible)	29.0	35.3	1.61	0.77	2.50

* Examples with different repeat compositions of 2,000 polymer preparations. T_b, T_m, ΔQ, ΔH, and ΔS are on-set temperature, maximum heat absorption temperature, heat, enthalpy, and entropy of the inverse temperature transition as determined by DSC, respectively. ΔH and ΔS are values per mole of repeating peptide. This is true for the DSC data reported in all tables in this article.

Table 3b. Effect of pH on inverse temperature transition of poly[0.82(GVGIP), 0.18(GEGIP)].[3]

pH	α^*	T_b (°C)	T_m (°C)	ΔQ (cal g^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} K^{-1})
2.3	0.00	10.3	12.9	4.00	1.71	5.92
3.5	0.04	15.2	18.2	2.80	1.20	4.10
4.2	0.11	20.7	24.9	1.51	0.64	2.14
4.6	0.13	24.0	32.0	1.19	0.51	1.66
5.1	0.20	26.0	37.0	0.60	0.26	0.83

* α is the degree of ionization of the Glu side chain.

Table 3c. Solute effect on inverse temperature transition.[2,5,12]

Polymer	Solute	δT_t (°C [M]$^{-1}$)	$\delta \Delta Q$ (cal g^{-1} [M]$^{-1}$)	Linearity
Poly(GVGVP)	Na_3PO_4 (pH > 8)	−140.0	–	Yes
	$(NH_4)_2SO_4$	−69.0	–	Yes
	Na_2CO_3 (pH > 8)	−28.0	–	Yes
	NaCl	−13.9	1.25	Yes
	$CaCl_2$	−6.6	–	Yes
	NaBr	−3.5	–	Yes
	NaI, NaSCN	3.5	–	No
	Sodium dodecyl sulfate	~600.0	–	–
Poly(GGIP)	NaCl	−13.4	1.35	Yes
Poly(GGVP)	NaCl	−15.6	0.52	Yes
Poly(GVGLP)	NaCl	−12.6	2.99	Yes
Poly(VPGVGVPGG)	NaCl	−15.9	0.96	Yes
Poly(AVGVP)	NaCl	−14.7	1.80	Yes

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Table 3d. Lowering transition temperature by charge neutralization.[5]

Polymer	[NaCl]/[N]	T_t (°C)	T_t (°C)
Poly[0.8(GVGVP), 0.2(GEGVP)]		pH < 3	pH > 7
	0.0	26.4	>100
	0.15	24.5	91.5
	0.20	–	73.7
	0.25	–	52.0
	0.50	19.9	47.0*
	1.0	13.6	35.8*
	1.5	–	26.0*
		$\delta T_t/[N] = -12.8$	$\delta T_t/[N]^* = -21.0$
Poly[0.85(GVGVP), 0.15(GDGVP)]		pH < 3	pH > 7
	0.0	28.3	>100
	0.15	24.5	75.0
	0.25	–	55.0
	0.50	21.5	50.3*
	0.75	–	44.0*
	1.0	15.5	40.0*
	1.5	–	31.0*
		$\delta T_t/[N] = -12.3$	$\delta T_t/[N]^* = -19.0$
Poly[0.76(GVGVP), 0.24(GKGVP)]		pH < 12	pH > 6
	0.0	30.4	>100
	0.05	–	70.0
	0.10	–	58.4
	0.125	–	53.0
	0.20	28.0	43.5
	0.25	–	35.2
	0.50	–	32.0*
	1.0	17.8	23.3*
	1.5	–	16.0*
		$\delta T_t/[N] = -12.6$	$\delta T_t/[N]^* = -16.0$

* Value for [NaCl] > 0.25; at lower salt concentration the slope is much steeper.

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Table 3e. Enhanced charge neutralization effect by $CaCl_2$ on lowering T_t.[5]

Polymer	$[CaCl_2]/[N]$	T_t (°C)	T_t (°C)
Poly[0.8(GVGVP), 0.2(GEGVP)]		pH = 2	pH = 7
	0.0	26.4	> 100.0
	0.0125	–	78.6
	0.025	–	70.0
	0.05	–	55.4
	0.1	25.5	51.5
	0.2	–	47.4*
	0.3	24.0	45.1*
	0.4	–	43.5*
	0.7	21.7	39.6*
		$\delta T_t/[N] = -6.8$	$\delta T_t/[N]^* = -13.6$

* Value for $[CaCl_2] > 0.1$; at lower salt concentration the slope is much steeper.

Table 3f. Urea and guanidine salt effect on inverse temperature transition.[5]

Polymer	Solute	Range [M]	$\langle \delta T_t \rangle^*$ (°C $[M]^{-1}$)	$\langle \delta \Delta Q \rangle$ (cal g^{-1} $[M]^{-1}$)	Linearity
Poly(GVGVP)	$Guanidine_2 \cdot H_2SO_4$ (pH 7.6)	[0, 1]	−11.4	1.06	Yes†
	Guanidine·HCl	[0, 2]	10.3	−1.01	Yes†
	Urea	[0, 3]	5.3	−0.57	Yes†
	Dimethyl urea	[0, 1]	12.2	−2.28	Yes
Poly(GVGIP)	$Guanidine_2 \cdot H_2SO_4$(pH 7.6)	[0, 1]	−8.9	0.76	Yes
	Guanidine·HCl	[0, 3]	6.8	−1.52	Yes†
	Urea	[0, 3]	4.0	−0.95	Yes

* $\langle \delta T_t \rangle$ = average slope over the listed range.
† With small nonlinearity.

Table 3g. Cosolvent effect on inverse temperature transition of poly(GVGVP) in water.[5]

Cosolvent	Volume (%)	T_b (°C)	ΔQ (cal g^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} K^{-1})
DMSO	35	16.7	0.38	0.15	0.53
	30	21.1	0.51	0.21	0.70
	20	29.5	0.91	0.37	1.21
	10	30.0	1.73	0.71	2.30
Acetone	20	31.8	0.99	0.40	1.30
	10	29.0	2.10	0.86	2.79
Dioxane	20	41.1	0.44	0.18	0.56
	10	31.6	1.42	0.58	1.87
H_2O		26.7	2.90	1.20	3.90

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Table 3h. Cosolvent effect on inverse temperature transition of poly(AVGVP) in water.[5]

Cosolvent	Volume (%)	T_b (°C)	ΔQ (cal g^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} K^{-1})
EtOH	15	27.2	4.51	1.91	6.31
	10	30.9	5.37	2.27	7.42
	5	32.8	6.65	2.81	9.14
Ethylene glycol	20	23.2	3.89	1.65	5.52
	10	29.6	5.54	2.35	7.70
Acetone	30	31.2	1.54	0.65	2.13
	20	32.7	3.31	1.40	4.55
H_2O		33.1	7.20	3.05	9.89

Table 3i. Cosolvent effect on inverse temperature transition of poly(GVGIP) in water.[5]

Acetone (volume %)	T_b (°C)	ΔQ (cal g^{-1})	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} K^{-1})
20	5.0	2.71	1.15	4.06
10	10.2	3.91	1.66	5.77
5	11.5	4.53	1.92	6.67
0	11.8	6.40	2.71	9.41

Table 3j. Solvent deuteration effect on inverse temperature transition.[13]

Polymer	Solvent	T_b (°C)	ΔQ (cal g^{-1})	ΔH (kcal mol^{-1})
Poly(GVGVP)	D_2O	27.2	3.25	1.33
	H_2O	28.8	2.62	1.07
Poly(GVGLP)	D_2O	13.7	6.70	2.83
	H_2O	15.5	6.02	2.55
Poly(GVGIP)	D_2O	9.0	6.76	2.86
	H_2O	10.6	6.17	2.61
Poly(AVGVP)	D_2O	31.7	7.17	3.04
	H_2O	34.2	6.46	2.73
	D_2O, 1.0 M urea	36.5	6.07	2.57
	H_2O, 1.0 M urea	38.5	5.27	2.23
	D_2O, 2.0 M urea	40.8	5.09	2.16
	H_2O, 2.0 M urea	43.0	4.37	1.85
	D_2O, 3.0 M urea	45.8	3.94	1.67
	H_2O, 3.0 M urea	48.5	3.55	1.51
	D_2O, 0.5 N NaCl	24.5	7.50	3.17
	H_2O, 0.5 N NaCl	26.1	6.93	2.93
	D_2O, 1.0 N NaCl	17.6	9.24	3.91
	H_2O, 1.0 N NaCl	19.1	8.79	3.72

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Table 3k. Alcohol effect on inverse temperature transition of poly(GVGVP) in water.[5]

Alcohol		T_b (°C)	ΔQ (J g^{-1})	ΔH (kJ g^{-1})	ΔS (J mol^{-1} K^{-1})
Mole %	Volume %				
Methanol					
16.01	30	13.6	1.21	0.50	1.67
10.0	20	23.5	3.47	1.42	4.73
4.71	10	27.8	7.07	2.89	9.46
2.29	5	28.2	9.87	4.06	13.18
Ethanol					
8.00	22	18.3	1.76	0.71	2.47
7.16	20	20.5	2.01	0.84	2.76
5.16	15	26.4	4.44	1.80	5.98
3.31	10	28.8	7.28	2.97	9.71
1.60	5	29.1	10.04	4.10	13.35
iso-Propanol					
5.55	20	18.4	3.01	1.21	4.14
3.26	15	26.0	4.56	1.84	6.19
2.08	10	28.1	7.70	3.14	10.33
n-Propanol					
5.69	20	11.9	3.51	1.42	4.94
4.08	15	19.8	7.03	2.89	9.71
2.61	10	25.5	9.50	3.89	12.80
tert-Butanol					
4.56	20	14.0	3.14	1.30	4.39
3.26	15	21.2	6.15	2.51	8.45
2.08	10	26.6	8.95	3.68	12.01
1.0	5	28.7	11.46	4.69	15.23
Ethylene glycol					
12.16	30	14.9	2.09	0.84	2.93
7.47	20	22.2	4.56	1.84	6.19
3.46	10	26.1	7.70	3.14	10.33
1.67	5	27.0	10.08	4.14	13.51
Glycerol					
9.57	30	9.4	6.53	2.68	9.25
5.82	20	20.1	7.28	2.97	10.00
2.67	10	24.2	9.04	3.68	12.22
1.28	5	26.4	10.50	4.31	14.06
H_2O		27.5	12.34	5.06	16.44

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Table 4. Physical properties of elastic and plastic protein-based polymers.

Polymer	Property	Conditions	Value
Elastic Polymer			
X^{20}-poly (GVGVP)[1]	Young's modulus	50% extension, 37°C	1.0×10^6
X^{20}-(GVGVP)251[1]	Young's modulus	50% extension, 37°C	1.6×10^6
	Max. extensibility (L/L_0)	–	>2.5
	Entropic elasticity (f_e/f)	–	<0.1
	Tensile strength	300% extension, 37°C	$3.1\,kg\,cm^{-2}$
X^{20}-poly (GVGIP)[1]	Young's modulus	90% extension, 37°C	3.9×10^6
	Max. extensibility (L/L_0)	–	>2.6
	Entropic elasticity (f_e/f)	–	<0.1
X^{20}-poly[3(GVGVP), (GFGVP)][1]	Young's modulus	80% extension, 37°C	4.9×10^6
	Transition temperature	$40\,mg\,ml^{-1}$ H_2O	13°C
	Max. extensibility (L/L_0)	–	>2
	Entropic elasticity (f_e/f)	–	<0.05
X^{20}-poly (GGVP)	Young's modulus	20% extension, 64°C	8.2×10^5
	Transition temperature	$40\,mg\,ml^{-1}$ H_2O	48°C
X^{20}-poly(VPGFGVGAG)[14]	Young's modulus	5% extension, 37°C	6.8×10^7
	Transition temperature	$40\,mg\,ml^{-1}$ H_2O	8°C
Plastic Polymer			
X^{20}-poly (AVGVP)[3]	Young's modulus	7% extension, 37°C	2.0×10^8
Hydrogel Polymer		Density ($mg\,ml^{-1}$)	
X^{20}-poly (GVGVP)[1]	<25°C	~40 at 4°C	
X^{20}-poly (GVGIP)[1]	<25°C	~80 at 4°C	
X^{20}-poly (AVGVP)[1]	<30°C	~40 at 4°C	
X^{20}-poly (GGXP), X = A, V, I	<50°C	~20 at 4°C	
Poly[0.8(AVGVP), 0.2(AFGVP)]	Forms gel at concentrations $>20\,mg\,ml^{-1}$ and > 18°C		
Poly (AVGIP)	Forms gel at concentrations $>20\,mg\,ml^{-1}$ and > 18°C		

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Table 5. Reversible contraction-relaxation of cross-linked polymer matrices.

Elastic polymer	Variable	Length
Thermally driven		
X^{20}-poly(GVGVP)[15]	40°C	4.4 cm
(3 g load)	20°C	5.4 cm
pH driven		
X^{20}-poly[0.8(GVGVP), 0.2(GEGVP)][2]	pH = 2	4.2 mm
(3 g load)	pH = 7	8.2 mm
Salt driven		
X^{20}-poly(GVGVP)[15]	1 N NaCl	5.15 cm
(at 20°C, 3 g load)	H_2O	5.50 cm
Organic solvent driven		
X^{20}-$(VPGVG)_{251}$[5]	H_2O	23.5 mm
(at 23°C, no load)	20 vol% EtOH	21.0 mm
Pressure driven	As in table 6	
Redox driven	As in table 6	

Table 6. Examples of free energy transduction effected by elastin protein-based polymers.

Transduction/Elastic polymer*	Intensive variable	Property measured
Thermo-mechanical	Temp. (°C)	Force (dynes cm^{-2})
X^{20}-poly(GVGVP)[16]	36	1.0×10^6
(at constant length)	5	4.0×10^5
X^{20}-poly[0.9(GVGVP), 0.1(GEGVP)][16]	37	2.3×10^6
(in pbs at 37°C, constant length.)	3	4.0×10^5
Chemo-mechanical	Chemical potential	Force (dynes cm^{-2})
X^{20}-poly[0.80(GVGVP), 0.20(GEGVP)][17]	pH = 2.1	5.1×10^5
(in pbs at 37°C, constant length.)	pH = 7.4	$< 1.0 \times 10^4$
X^{20}-poly(GVGVP)[18]	[0.15 N NaCl, 0.01 M phosphate]	2.1 g
(at 25°C, constant length)	H_2O	0
Baro-mechanical	Pressure (atm)	Length (mm)
Poly[0.79(GVGVP), 0.21(GVGFP)][19,20]	68	(16.2)[19], (38.5)[20]
(at 12.6°C, 1 gram constant force)	1	(15.2)[19], (37.0)[20]
Electro-mechanical	Redox	Length (mm)
X^{20}-poly[0.70(GVGVP), 0.30(GVGK{NMeN}P)][20]	Reduced	(3.2)[20], (1.92)[21]
		(4.0)[20], (2.16)[21]
X^{20}-poly[0.73(GVGVP), 0.27(GVGK{NMeN}P)][21]	Oxidized	
Photo-mechanical	Photon	T_t (°C)
Poly[0.8(GVGVP), 0.2(GVGE{AzB}P)][22]	Dark	32
	350 nm light	42

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Table 6. Continued

Transduction/Elastic polymer*	Intensive variable	Property measured
Mechano-chemical	Mechanical force	pK of Glu(E)
X^{20}-poly[0.82(GVGIP), 0.18(GEGIP)][11]	0	6.2
	8.0×10^5 (dynes cm^{-2})	9.0
Electro-chemical	Redox	pK of Asp(D)
Poly(GDGFP GVGVP GVGVP GFGVP GVGVP	Reduced	11.0
GVGK{NMeN}P)[23]	Oxidized	8.5

*K{NMeN} = N-methyl nicotinamide derivatised Lys; E{AzB} = azobenzene derivatized Glu.

Table 7. Physical properties of the synthetic poly(W4)* from human elastin.[24]

Polymer	Condition	T_b (°C)	ΔQ (cal g^{-1})	ΔH (kcal mol^{-1})†	ΔH (kcal mol^{-1})‡	ΔS (kcal mol^{-1} K^{-1})‡
Poly(W4)	pH = 2.0	25.5	1.92	0.86	8.79	28.63
	pH = 4.3	27.8	1.45	0.65	6.63	21.43
	pH = 5.8	28.0	0.32	0.14	1.48	4.62
	pK of the Glu = 4.84					
X^{20}-poly(W4)	Young's modulus = 3.4×10^5 dynes cm^{-2} at 37°C in pbs					
	Entropic elasticity indicated by a f_e/f value of < 0.1 from 35 to 50°C					

*W4(6-56): GLVPGGPGFPGGVVGVPGAGVPGVGVPGAGIPVVPGAGIPGAAVPGVVSPE.
†Per mole of pentapeptide.
‡Per mole of W4.

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Epoxy resins

MEE Y. SHELLEY

TRADE NAMES Araldite, DER, Epi-Cure, Epi-Res, Epikote, Epon, Epotuf, etc.

CLASS Thermoset polymers, after curing (the uncured base resins are thermoplastic)

MAJOR RESIN TYPES DGEBA (diglycidyl ether of bisphenol A), novolacs, peracid resins, hydantoin resins, etc.

OTHER INGREDIENTS IN EPOXY FORMULATION Diluents, resinuous modifiers (to affect flexibility, toughness, peel strength, adhesion, etc.), fillers, colorants and dyes, other additives (e.g., rheological additives, flame retardants).

MAJOR APPLICATIONS Protective coatings (for appliance, automotive primers, pipes, etc.). Encapsulation of electrical and electronic devices. Adhesives. Bonding materials for dental uses. Replacement of welding and riveting in aircraft and automobiles. In composites for materials in space industry, printed circuitry, pressure vessels and pipes. Construction uses such as flooring, paving, and airport runway repair.

PROPERTIES OF SPECIAL INTEREST Wide range of properties depending on the formulation and processing. Chemical and weathering resistance, toughness, durability. Excellent adhesion to a variety of surfaces. Good electrical and thermal insulation. Better mechanical properties than most other castable plastics. Discolor when exposed to UV. Some are skin sensitizers.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Specific gravity	—	Unfilled	1.2–1.3	(1)
		Bisphenol molding compounds (glass fiber-reinforced/ mineral-filled)	1.6–2.1	(2)
		Bisphenol molding compounds (low density glass sphere-filled)	0.75–1.0	(2)
		Sheet molding compounds	0.1	(2)
		Novolac molding compounds	1.6–2.05	(2)
		Casting resins, silica-filled	1.6–2.0	(2)
		Casting resins, aluminum-filled	1.4–1.8	(2)
		Casting resins, flexibilized	0.96–1.35	(2)
		Casting resins, cycloaliphatic	1.16–1.21	(2)
Water absorption	%	1/8 in. thick specimen, 24 h		
		Bisphenol molding compounds	0.04–1.0	(2)
		Sheet molding compounds	1.4–1.6	(2)
		Novolac molding compounds	0.04–0.29	(2)
		Casting resins, silica-filled	0.04–0.1	(2)
		Casting resins, aluminum-filled	0.1–4.0	(2)
		Casting resins, flexibilized	0.27–0.5	(2)
		Filament wound (80 wt% glass fiber-reinforced)	0.50	(3, 4)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Impact strength, Izod	$J\,m^{-1}$	Unfilled	10–50	(1)
		Silica-filled	16–24	(2)
		Aluminum-filled	21–85	(2)
		Flexibilized	120–270	(2)
		Bisphenol molding compounds (glass fiber-reinforced)	16–530	(2)
		Bisphenol molding compounds (mineral-filled)	16–27	(2)
		Bisphenol molding compounds (low density glass sphere-filled)	8–13	(2)
		Sheet molding compounds (glass fiber-reinforced)	1,600–2,100	(2)
		Sheet molding compounds (carbon fiber-reinforced)	800–1,100	(2)
		Novolac molding compounds	16–27	(2)
		Filament wound (80 wt% glass fiber-reinforced)	2,400	(3, 4)
Hardness	Shore	Casting resins, flexibilized	D65–89	(2)
	Barcol	Novolac molding compounds	70–78	(2)
	Rockwell	Filament wound (80 wt% glass fiber-reinforced)	M98	(3, 4)
Fracture toughness	$J\,cm^{-3}\,m^{1/2}$	Unspecified	0.6	(1)
Tensile modulus	MPa	Unfilled	3,000–5,000	(1)
		Casting, unfilled	2,400	(2)
		Bisphenol molding compounds (glass fiber-reinforced)	21,000	(2)
		Bisphenol molding compounds (mineral-filled)	2,400	(2)
		Sheet molding compounds (glass fiber-reinforced)	14,000–28,000	(2)
		Sheet molding compounds carbon fiber-reinforced)	70,000	(2)
		Novolac molding compounds	14,500–16,600	(2)
		Filament wound (80 wt% glass fiber-reinforced)	27,600	(3, 4)
Compressive modulus	MPa	Casting, flexibilized	7–2,400	(2)
		Casting, cycloaliphatic	3,400	
		Bisphenol molding compounds (mineral-filled)	4,500	
		Novolac molding compounds (mineral- and glass-filled, high temperature)	4,550	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Stress at break	MPa	Unfilled	30–90	(1)
Tensile strength at break	MPa	Casting resins, unfilled	28–90	(2)
		Casting resins, silica-filled	48–90	(2)
		Casting resins, aluminum-filled	48–83	(2)
		Casting resins, flexibilized	14–70	(2)
		Casting resins, cycloaliphatic	55–83	(2)
		Bisphenol molding compounds (glass fiber-reinforced/mineral-filled)	28–140	(2)
		Bisphenol molding compounds (low density glass sphere-filled)	17–28	(2)
		Sheet molding compounds (glass fiber-reinforced)	140–240	(2)
		Sheet molding compounds (carbon fiber-reinforced)	280–340	(2)
		Novolac molding compounds	34–110	(2)
		Filament wound (80 wt% glass fiber-reinforced)	552	(3, 4)
Elongation at break	%	Unfilled	1–2	(1)
		Bisphenol molding compounds (filled with glass fiber)	4	(2)
		Sheet molding compounds	0.5–2	(2)
		Casting resins, unfilled	3–6	(2)
		Casing resins, aluminum-filled	0.5–3	(2)
		Casing resins, silica-filled	1–3	(2)
		Casing resins, flexibilized	20–85	(2)
		Casing resins, cycloaliphatic	2–10	(2)
		Filament wound (80 wt% glass fiber-reinforced)	1.6	(3, 4)
Flexural strength	MPa	Bisphenol molding compounds	34–200	(2)
		Sheet molding compounds	340–660	
		Novolac molding compounds	70–150	
		Casting resins and compounds	55–170	
Flexural modulus	MPa	Bisphenol molding compounds	3,400–31,000	(2)
		Sheet molding compounds	14,000–34,000	(2)
		Novolac molding compounds	9,700–17,000	(2)
		Filament wound (80 wt% glass fiber-reinforced)	34,500	(3, 4)
Compressive strength	MPa	Casting, unfilled	100–170	(2)
		Casting, silica or alumina-filled	100–240	(2)
		Casting, flexibilized	7–97	(2)
		Casting, cycloaliphatic	100–140	(2)
		Bisphenol molding compounds (glass fiber-reinforced/mineral-filled)	120–280	(2)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Compressive strength	MPa	Bisphenol molding compounds (low density glass sphere-filled)	70–100	(2)
		Sheet molding compounds (glass fiber-reinforced)	140–210	(2)
		Sheet molding compounds (carbon fiber-reinforced)	210–280	(2)
		Novolac molding compounds	170–330	(2)
		Filament wound (80 wt% glass fiber-reinforced)	310	(3, 4)

Surface tension

Polymer	Temp. (K)	Value ($mN\,m^{-1}$)	Reference
DGEBA with 6 wt% N-N-diethylaminopropylamine, cured	293	46.8	(5)
DGEBA with stoichiometric amount of triethylenetetramine, cured	293	39.1	(5)
DGEBA, 2,3-(diglycidoxy-1,4-phenylene)propane, chain extended with bisphenol A	296	51.2	(5, 6)

Interfacial tension[(5)]

Polymer	Temp. (K)	Value ($mN\,m^{-1}$)
Poly(butadiene) vs. epoxy resin*	296	1.77
	328	1.40
Poly(butadiene-stat-acrylonitrile) 18 wt% AN vs. epoxy resin*	293	1.23
	328	0.57
Poly(butadiene-stat-acrylonitrile) 26 wt% AN vs. epoxy resin*	328	0.58

*Epoxy resin: DGEBA, chain extended with bisphenol A.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Volume resistivity	ohm cm	Filled with glass	10^{16}	(7)
		Filled with mineral	10^{16}	
Dielectric strength	$V\,mil^{-1}$	Filled with glass	360	(7)
		Filled with mineral	400	
Dielectric constant		At 1 MHz		(7)
		Filled with glass	4.6	
		Filled with mineral	5.0	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Thermal conductivity	$W m^{-1} K^{-1}$	Casting grade, 293 K	0.19	(8, 9)
		Casting grade, 300–500 K	0.19–0.34	(9, 10)
		Foam, $d = 0.032–0.048\ g\ cm^{-3}$	0.016–0.022	(9, 11)
		Foam, $d = 0.080–0.128\ g\ cm^{-3}$	0.035–0.040	(9, 11)
		Filled with 50% aluminum	1.7–3.4	(9, 12)
		Filled with 25% Al_2O_3	0.35–0.52	(9, 12)
		Filled with 50% Al_2O_3	0.52–0.69	(9, 12)
		Filled with 75% Al_2O_3	1.4–1.7	(9, 12)
		Filled with 30% mica	0.24	(9, 8)
		Filled with 50% mica	0.39	(9, 8)
		Filled with silica	0.42–0.84	(9, 8, 12)
		Filament wound (80 wt% glass fiber-reinforced)	1.77	(3, 4)
Deflection temperature	K	Under flexural load, 1.82 MPa		(2)
		Bisphenol molding compounds, glass fiber-reinforced/mineral-filled	380–530	
		Bisphenol molding compounds, low density glass sphere-filled	370–390	
		Sheet molding compounds	560	
		Novolac molding compounds	420–530	
		Casting resins and compounds (unfilled)	320–560	
		Casting resins and compounds (silica-filled)	340–560	
		Casting resins and compounds (aluminum-filled)	360–590	
		Casting resins and compounds (flexibilized)	296–390	
		Casting resins and compounds (cycloaliphatic)	370–510	

Radiation resistance, half-value dose in air*

Conditions	Dose rate ($Gy\ h^{-1}$)	Value (MGy)	Reference
Filled with glass fiber	$\geq 10^5$	25–100+	(13, 14)
Filled with graphite	$\geq 10^5$	50	(13, 14)
Filled with mineral flour	$\geq 10^5$	10–30	(13, 14)
Filled with mineral flour (85% quartz sand)	500	7	(13, 15)
Filled with cotton	$\geq 10^5$	1	(13, 14)

*Defined as the absorbed dose that reduces a property (flexural strength) to 50% of the initial value.

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Solubility parameters	$(MPa)^{1/2}$			
Hildebrand parameter δ		–	22.3	(16, 17)
Hansen parameters		Epikote 1001 (Shell)		(17, 18)
δ_d			20.36	
δ_p			12.03	
δ_h			11.48	
δ_t			26.29	
Processing temperature	K	Bisphenol molding compounds		(2)
		Compression	390–440	
		Transfer	390–470	
		Sheet molding compounds		
		Compression	390–440	
		Transfer	405–440	
		Novolac molding compounds		
		Compression	410–460	
		Injection	420–450	
		Transfer	390–480	
Molding pressure	MPa	Bisphenol molding compounds	0.7–34	(2)
		Sheet molding compounds	3.4–14	
		Novolac molding compounds	1.7–21	
Compression ratio	–	Bisphenol molding compounds	2.0–7.0	(2)
		Sheet molding compounds	2.0	
		Novolac molding compounds	1.5–2.5	
Mold shrinkage (linear)	–	Bisphenol molding compounds	0.001–0.01	(2)
		Sheet molding compounds	0.001	
		Novolac molding compounds	0.004–0.008	
		Casting resins	0.0005–0.01	

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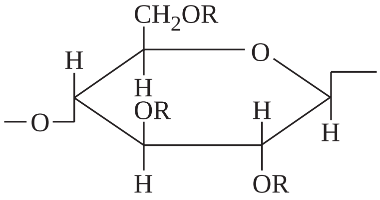
Ethylcellulose

YONG YANG

ACRONYM EC

CLASS Carbohydrate polymers

STRUCTURE



(R is CH_2CH_3 or H)

MAJOR APPLICATIONS Lacquers for wood, plastic, and paper, varnishes, hot melts, adhesives, thickener in coatings and inks, tablet coatings and binding, encapsulation.

PROPERTIES OF SPECIAL INTEREST Low temperature flexibility, soluble in a variety of organic solvents.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	—	Degree of substitution (DS) = 3.0	246.30	—
Preparation	Cellulose + NaOH → Na-cellulose (alkali cellulose) Na-cellulose + C_2H_5Cl → Ethyl cellulose + NaCl			(1)
IR (characteristic absorption frequencies)	cm^{-1}	Assignment		(2, 3)
		(C_2H_5) stretching	2,970	
		(C_2H_5) stretching	2,870	
		(C_2H_5) stretching	2,900	
		(C_2H_5) stretching	2,870	
		(C_2H_5) deformation	1,490	
		(C_2H_5) deformation	1,450	
		(C_2H_5) deformation	1,410	
		(C_2H_5) deformation	1,380	
		(C_2H_5) deformation	1,320	
		(C_2H_5) deformation	1,280	
		(C–O) stretching	1,109	
Thermal expansion coefficient	K^{-1}	Sheet	$(10–20) \times 10^{-5}$	(4)
Specific gravity	$g\ cm^{-3}$	—	1.14	(1)

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Solubility parameters δ	$(MPa)^{1/2}$	Solvent	DS	Temp. (K)		
		–	2.4–2.6	–	21.1	(5)
		Poor H-bonding solvent	2.4–2.6	–	20	(6)
			–	–	16.6–22.7	(7)
			2.6–2.8	–	17.4–19.4	(7)
		Moderate H-bonding solvent	2.4–2.6	–	21	(6)
			–	–	15.1–22.2	(7)
		Strong H-bonding solvent	2.4–2.6	–	19.4–29.7	(7)
			2.6–2.8	–	19.4–23.3	(7)
		Acetone	2.5	298	19.4	(8)
		n-Amyl acetate	2.5	298	18.7	(8)
		Benzene	2.5	298	20.6	(8)
		n-Butyl acetate	2.5	298	18.7	(8)
		Ethyl acetate	2.5	298	19.1	(8)
		Methyl acetate	2.5	298	19.3	(8)
		Methyl *n*-amyl ketone	2.5	298	18.8	(8)
		Methyl ethyl ketone	2.5	298	19.1	(8)
		Methyl *n*-propyl ketone	2.5	298	19.0	(8)
		n-Propyl acetate	2.5	298	18.8	(8)
		Tetrachloromethane	2.5	298	20.6	(8)
		Toluene	2.5	298	20.4	(8)
		Trichloromethane	2.5	298	18.6	(8)
Polymer-liquid interaction parameter χ	–	Solvent	DS	Temp. (K)		(8, 9)
		Acetone	2.45	298	0.46	
		n-Amyl acetate	2.45	298	0.28	
		Benzene	2.45	298	0.48	
		n-Butyl acetate	2.45	298	0.24	
		Ethyl acetate	2.45	298	0.40	
		Methyl acetate	2.45	298	0.41	
		Methyl *n*-amyl ketone	2.45	298	0.38	
		Methyl ethyl ketone	2.45	298	0.42	
		Methyl *n*-propyl ketone	2.45	298	0.37	
		n-Propyl acetate	2.45	298	0.33	
		Tetrachloromethane	2.45	298	0.46	
		Toluene	2.45	298	0.47	
		Trichloromethane	2.45	298	0.34	
		Water	1.4	328	1.1	

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Solvents and nonsolvents[1,10,11]

DS	Solvent	Nonsolvent
0.5–0.7	Aqueous alkali	Water
1.0–1.5	Acetic acid, formic acid, pyridine, water (cold)	Ethanol
2	Chloroform, chlorohydrins, dichloroethylene, ethanol, methylene chloride, tetrahydrofuran	Alcohols, carbon tetrachloroethylene, diethyl ether, esters, ketones, hydrocarbons, water
2.3	Acetic esters, alcohols, alkyl halogenids, benzene, carbon disulfide, furan derivatives, ketones, nitromethane	Acetone (cold), ethylene glycol
2.4–2.6	Acetic acid*, acetone, amyl acetate, amyl alcohol, benzene, benzyl acetate, benzyl alcohol, butanol, butyl acetate, butyl lactate, carbon tetrachloride*, chloroform*, *m*-cresol*, cyclohexanol, cyclohexanone, dichloroacetic acid*, dichloromethane*, 1,5-dimethyl-2-pyrrolidone*, dioxane, ethanol, ethylene chloride, ethyl acetate, ethyl ether, ethyl formate, ethyl lactate, formic acid*, hexone, methanol, methyl ethyl ketone, methylene dichloride, methyl formate, 1-nitropropane, 2-nitropropane, phenol*, propanol, propyl acetate, toluene, trichloroethylene*, trifluoroacetic acid*, trifluoroethanol*, xylene	Hexane, nitromethane, petroleum ether
3	Alcohols, ester, benzene, methylene chloride	Carbon tetrachloride, diols, hydrocarbons, *n*-propyl ether, tetrahydrofurfuryl alcohol

*Forms liquid crystal mesophase.

Mark-Houwink parameters: K and a[12]

Solvent	Temp. (K)	$M_w \times 10^{-4}$ (g mol^{-1})	Method	$K \times 10^3$ (ml g^{-1})	a
Acetone	293	8	Osmometry	1.51	1.05
Benzene	293	8	Osmometry	1.34	1.07
	298	14	Osmometry	29.2	0.81
	333	14	Osmometry	35.8	0.78
Butanone	298	14	Osmometry	18.2	0.84
	333	14	Osmometry	26.7	0.79
Butyl acetate	298	14	Osmometry	14.0	0.87
	333	14	Osmometry	18.1	0.83
Chloroform	298	14	Osmometry	11.8	0.89
	319	14	Osmometry	9.3	0.90
Ethyl acetate	298	14	Osmometry	10.7	0.89
	333	14	Osmometry	14.0	0.85
Methanol	298	14	Light scattering	52.3	0.65
Nitroethane	298	14	Osmometry	4.2	0.96
	333	14	Osmometry	22.6	0.79

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Ethylcellulose

Unit cell dimension of triethylcellulose[13]

Lattice	Monomers per unit cell	Chains per unit cell	Cell dimension (Å)			Density ($g\ cm^{-3}$)	Chain conformation
			a	*b*	*c*		
Orthorhombic	12	6	15.64	27.09	15.0	1.158	3_2

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Martin coefficient k'	–	Toluene/ethanol (80/20)	0.111	(14)
Glass transition temperature	K	–	316	(15)
		DS = 2.45–2.60	393–397	(1)
Heat capacity (of repeat unit)	$kJ\ K^{-1}\ mol^{-1}$	–	0.31–0.77	(4)
Deflection temperature	K	1.82 MPa	319–362	(4)
Tensile modulus	MPa	–	897–2,069	(4)
Tensile strength	MPa	–	14–55	(4)
			47–72	(1)
Maximum extensibility	%	–	15–100	(4)
		Conditioned at 298 K, 50% RH	7–30	(1)
Compressive strength	MPa	ASTM D695	69–241	(4)
Flexural yield strength	MPa	–	28–83	(4)
Flexural strength	MPa	–	62–69	(16)
Impact strength	$J\ m^{-1}$	0.5 × 0.5 in notched bar, Izod test, ASTM D256		(4)
		Molding	107–455	
		Sheet	16–91	
Hardness	–	Rockwell, R scale	50–115	(4)
		Sward, 3-mil film	52–61	(1)
Index of refraction n	–	–	1.47	(4)
Refractive index increment dn/dc	$ml\ g^{-1}$	MeOH, $\lambda = 436$ nm, 298 K	0.130	(17)
Dielectric constant ε''	–	298 K, 1 MHz	2.8–3.9	(1)
		298 K, 1,000 Hz	3.0–4.1	
		298 K, 60 Hz	2.5–4.0	
Power factor	–	298 K, 1 Hz	0.002–0.02	(1)
		298 K, 60 Hz	0.005–0.02	

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Resistivity	ohm cm^{-1}	–		10^{12}–10^{14}	(1)
Surface tension	mN m^{-1}	Contact angle		32	(18)
Thermal conductivity	W m^{-1} K^{-1}	–		0.21	(19)
Water absorption	%	24 h at 50% RH		2	(1)
Permeability coefficient *P*	m^3(STP) m s^{-1} m^{-2} Pa^{-1} ($\times 10^{17}$)	Permeant	Temp. (K)		(20)
		H_2	293	65.3	
		He	298	40.1	
		N_2	298	3.32	
		O_2	298	19.0	
		Ar	298	7.65	
		CO_2	298	84.8	
		SO_2	298	198	
		NH_3	298	529	
		H_2O	298	6700	
		C_2H_6	298	6.9	
		C_3H_8	298	2.78	
		n-C_4H_{10}	298	2.9	
		n-C_5H_{12}	298	2.78	
		n-C_6H_{14}	298	5.75	
Cost	US\$ kg^{-1}	–		17.5–26	–
Supplier	Hercules Inc., 1313 North Market Street, Wilmington, Delaware 19894, USA				

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Ethylene-propylene-diene monomer elastomers

GARY W. VER STRATE AND DAVID J. LOHSE

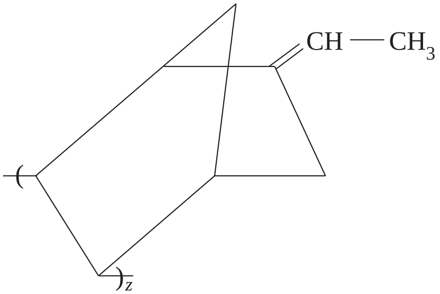
ACRONYMS, ALTERNATIVE NAME EP, EPM, EPR (as copolymer), EPDM (contains a third monomer, which provides up to 10 weight % of an olefin site for cross-linking), ethene-propene-diene elastomers.(1–5)

CLASS Chemical copolymers; polyolefin copolymer; ter-polymer elastomer

STRUCTURE

$-\!\!(CH_2-CH_2)_x- \quad -\!\!(CH_2-CH(CH_3))_y-$

ENB shown as third monomer(2–4)



PROPERTIES OF SPECIAL INTEREST High plateau modulus (1.6 MPa) permits high filler loadings and cost-effective compounds, chemically inert, semicrystalline grades have high green strength.(2, 3, 6)

PREPARATIVE TECHNIQUES Type of polymerization: Ziegler-Natta or metallocene (e.g., $VOCl_3/Et_3Al_2Cl_3$, 30–70°C, hydrocarbon solution, or Cp_2Zr/methalumoxane, hydrocarbon solution, 80–120°C.(2–6)

TYPICAL COMONOMERS Ethene, propene, ethylidene norbornene (ENB) or dicyclopentadiene or (DCPD), 1,4 hexadiene (4,4 HD), or vinyl norbornene (VNB) or norbornadiene (NBD).(2–7)

Ziegler-Natta gives better incorporation of bicyclic dienes than metallocenes; for straight-chain dienes the reverse is true.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Ceiling temperature	K	Polymerization at <1 MPa up to this temperature is possible	>440	(6)
Molecular weight (of repeat unit)	$g\,mol^{-1}$	50 mol% ethene, 1 mol% diene	~35 (average)	(2–5)
Tacticity (stereoregularity)	% stereo-regular propene in elastomer grades	Vanadium or metallocene catalysis	0	(2–5, 8)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Head-to-head contents	%	Vanadium or metallocene catalysis	<3	(2–5, 8)
Degree of branching	% of molecules having long branches	Vanadium catalysis mostly by cationic diene coupling; metallocene by end group copolymerization; can be controlled (information available from manufacturers)	0–100	(2–5)
Typical molecular weight range of polymer $\bar{M}_n$	$g\,mol^{-1}$	500–5,000 as dispersants 2,000–300,000 as elastomers 5,000–5,000,000 in blends	–	(2–5, 7)
Typical polydispersity index (M_w/M_n)	Dimensionless	Controlled by catalyst choice, reactor type	1.5–50	(2–5)
Morphology in multiphase systems	As shown	Semicrystalline copolymers, blends, block copolymers Lamellae, width Lamellae, length Elastomer blends, major dimension	 50–150 Å 0.01–2 μm 0.5–10 μm	(2–4, 9, 10)
IR (characteristic absorption frequencies)	cm^{-1}	20°C, films $-CH_2$ Isopropyl $-CH_3$ $-CH_3$	 720 1,145 1,370	(2–4, 11)
UV (characteristic absorption frequencies)	nm	20°C in solution (broad, maximum, depends on diene type)	<200	(2–4)
NMR	ppm (chemical shift)	^{13}C, ^{1}H (see references for extensive detailed work)	Specific carbons or protons have specific shifts	(3, 8)
Thermal expansion coefficients	K^{-1}	1 atmosphere, no crystallinity $(1/V)(dV/dT)_P$	7×10^{-4}	(2, 12, 13)
Compressibility coefficients	bar^{-1}	20°C $(1/V)(dV/dP)_T$	5.8×10^{-8}	(2, 12, 13)
Reducing temperature T^*	K	150–250°C, 10–200 MPa	6,800	(12)
Reducing pressure P^*	MPa	150–250°C, 10–200 MPa	444–465	(12)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Reducing volume V^*	$cm^3\ g^{-1}$	150–250°C, 10–200 MPa	1.000	(12)
Density (amorphous)	$g\ cm^{-3}$	20°C, no diene present, <55 wt% ethene, the dienes ENB, DCPD, and VNB raise density as does crystallinity	0.854	(2, 12)
Solvents	–	Ambient	Aliphatic, aromatic, halogenated hydrocarbons	(2, 3, 14)
Nonsolvents	–	Ambient	Water, organic acids, ketones, polar halogenated hydrocarbons	(2, 3, 14)
Solubility parameter	$(MPa)^{1/2}$	By SANS (depending on ethene %)	16–17	(13)
		By GLC	16	(15)
Theta temperature Θ	K	Phenyl ethyl ether, depends on exact composition	353	(2, 3, 14, 16–18)
		n-Octyl acetate	300	
		n-Decyl acetate	278	
		n-Hexyl acetate	334	
Interaction parameter χ	Dimensionless	*n*-Heptane, 300 K	$(0.35 + 0.08 \times V_{polymer})$	(2, 3, 14)
Second virial coefficient	$mol\ cm^3\ g^{-2}$	Trichlorobenzene, 135°C	$(9.9 \times 10^{-3})M^{-0.18}$	(3, 19)
Mark-Houwink parameters: K and a	$K = ml\ g^{-1}$ $a =$ None	Trichlorobenzene, 135°C	$K = 2.9 \times 10^{-2}$ $a = 0.726$	(3, 19)
Huggins constants k'	–	Theta solvents, depends on polymer molecular weight	0.4–0.8	(18)
Characteristic ratio $\langle r^2 \rangle_0/nl^2$	–	Phenyl ethyl ether, 80°C	6.9	(16)
		SANS, 20°C	6.9	(17)
Lattice	–	Methylene units crystallize into a polyethene lattice, methyl groups can incorporate somewhat	Orthorhombic	(2, 14)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Unit cell dimensions	Å	1 atm, 20°C, $-CH_2-$ sequences only, methyl group causes expansion	$a = 7.418$ $b = 4.946$ $c = 2.546$	(2, 3, 14, 20)
Unit cell contents	Number of mers	Ethene crystallinity	2	(2, 3, 14, 20)
Degree of crystallinity	%	Depends on ethene content	0–50	(2, 3)
Heat of fusion (of repeat units)	$kJ\,mol^{-1}$ $cal\,g^{-1}$	DSC on samples annealed at 20°C >48 h, varies with ethene content	0–4.4 0–35	(2, 3)
Density (crystalline)	$g\,cm^{-1}$	1 atm, 20°C	0.997 (can be reduced by defects to 0.99 and below)	(2, 3, 20)
Glass transition temperature	K	1 atm, DSC, dynamic mechanical, depends on ethene content, lowest at about 50% ethene; crystallinity confuses the issue at high ethene contents	213–240	(2, 3, 21)
Melting point	K	1 atm, DSC, depends on ethene content; often melts just above last annealing temperature; will crystallize down to T_g	218–373	(2, 3)
Heat capacity (of repeat units)	$kJ\,K^{-1}\,mol^{-1}$	DSC, 1 atm	0.078	(2, 3, 12)
Polymers with which miscible	–	MW < 150,000 MW < 100,000	Head-to-head polypropylene Ethylene-butene copolymers of similar comonomer content	(22)
Tensile modulus	MPa	20°C, low strain rate, filled compound 25% rubber, 50% carbon black, 25% oil tested at $\sim 1\,s^{-1}$	3–7	(2, 3, 6, 23)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Shear modulus	MPa	20°C, low strain rate, filled compound 25% rubber, 50% carbon black, 25% oil	1–4	(2, 3, 6, 23)
Storage modulus	MPa	High molecular weight gum rubber, 20°C, 1 Hz	0.16	(6, 15)
Loss modulus, tan δ	–	High molecular weight gum rubber, 20°C, 1 Hz	0.2	(6, 15)
Tensile strength	MPa	Dependent on compounding and test conditions, typical compounds at 20°C, 1 s^{-1}	0.5–50 5–25	(2, 3, 6, 23, 24)
Maximum extensibility $(L/L_0)_r$	%	Dependent on compounding and test conditions	200–800	(2, 3, 6, 23)
Hardness	Shore A values	Dependent on compounding and test conditions	10–100	(2, 3, 23)
Poisson's ratio	–	0–50°C, strained at 100 s^{-1} or less	0.49	(6, 11)
Plateau modulus	MPa	20–150°C	1.6	(6, 15)
Entanglement molecular weight	g mol^{-1}	20°C, $M_e = \rho RT\ G_N^\circ$	1,300	(2, 3, 6, 21)
WLF parameters: C_1 and C_2	C_1 = None C_2 = K	T_0 = 300 K, depends on composition	$C_1^\circ = 5.4, 4.1$ $C_2^\circ = 148, 122$	(3, 6, 21, 25)
Index of refraction n_D	–	1 atm, no diene, 23°C No crystallinity, 90°C 125°C	1.4740 1.4524 1.4423	(2, 3)
Refractive index increment dn/dc	ml g^{-1}	Trichlorobenzene, 135°C	−0.104	(3)
Dielectric constant ε'	–	20°C, 10^3 Hz, 1 atm, depends on the compound, a good insulator	2.8	(2, 3, 14, 23)
Dielectric loss ε''	–	20°C, 10^3 Hz, 1 atm, depends on the compound	0.2 0.25	(2, 3, 14)
Resistivity	log R, ohm cm	1 atm, 20°C, depends on compound, generally a good insulator	3–14	(2, 14, 26–28)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molar polarizability α	cm^3	Frequency	4.4×10^{-26}	(2, 3)
Surface tension	$mN\,m^{-1}$	20°C, 1 atm, increases with ethene content	29.4–36.8	(28, 29)
Interfacial tension	$mN\,m^{-1}$	With PDMS, 20°C With PS, 140°C	3.2–5.3 5.1–5.9	(28, 29)
Permeability coefficient	$([m^3]\,[m])/([S]\,[m^2]\,[^T Pa])$	He 25°C N_2 25°C	16.0–24.0 $(\times 10^{-17})$ 3.7–4.1 $(\times 10^{-17})$	(30)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	20°C, 1 atm	0.355	(2, 3, 31)
Melt viscosity	Pa s	Newtonian at 100°C	$(4 \times 10^{-5})M^{3.6}$	(3, 21)
Melt index	g	2.2 kg, 190°C, depends completely on polymer molecular weight	0.001–50	(2, 3, 23)
Mooney viscosity	Mooney units	125°C	5-100	(2, 3, 23)
Pyrolyzability, amount of product remaining	%	>500°C	<0.3%	(2, 3, 32)
Severe decomposition	K	N_2 blanket	580	(2, 32)
Maximum use temperature	K	Open atmosphere	450	(2, 3, 23)
Decomposition temperature	K	Nitrogen atmosphere, 1 minute	570	(2, 3, 32)
Scission, *G* factor, $G(s)$	$mol\,J^{-1}$	γ irradiation, depends on ethene and diene content	1.1–5.9 $(\times 10^{-8})$	(2, 24, 33)
Cross-linking, *G* factor, $G(x)$	$mol\,J^{-1}$	γ irradiation, depends on ethene and diene content	2.7–22.6 $(\times 10^{-8})$	(2, 24, 33)
Gas evolution, *G* factor, *G*(gas)	$mol\,J^{-1}$	γ irradiation, depends on ethene and diene content	3.4×10^{-7}	(24)
Water absorption	% volume increase % tensile change	168 h, 55% ethylene glycol in water, boiling	+1 −1	(23)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Cost	US\$ kg^{-1}	–	2.60	(34–36)
Availability	–	–	ktons	(3, 34–36)
Suppliers	Exxon Chemical; DSM; JSR; Mitsui; DuPont-Dow; Uniroyal; Bayer			(3, 35)

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Ethylene-vinyl acetate copolymer

PING XU

ACRONYMS, TRADE NAMES EVA; A-C® (Allied Signal); Elvax® (DuPont); Levapren® (Bayer); Microthene®, Spectratech®, Ultrathene® (Quantum Chemical); Modic®, Novatec® (Mitsubishi Kasei); PDX® (LNP)

CLASS Chemical copolymers

STRUCTURE $[-CH_2-CH_2-]_m-[-CH_2-CH(-O-C(=O)-CH_3)-]_n$

MAJOR APPLICATIONS Film extrusion, packaging, wire and cable insulation, adhesives, coatings, and compounding.

PROPERTIES OF SPECIAL INTEREST Flexibility and toughness, good adhesion, and stress crack resistance.

PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Linear thermal expansion coefficient	K^{-1}	ASTM D696, no composition given	$16–25 \times 10^{-5}$	(1)
Density	$g\,cm^{-3}$	ASTM D792, 9–28% vinyl acetate	0.93–0.95	(2)
Solubility parameter	$(MPa)^{1/2}$	Halogenated aliphatic and aromatic liquids, 20°C		(3)
		30% vinyl acetate	19.0	
		40% vinyl acetate	19.2	
		67% vinyl acetate	19.0	
		Halogenated aliphatic and aromatic liquids, 30°C		
		30% vinyl acetate	18.8	
		40% vinyl acetate	18.9	
		67% vinyl acetate	18.9	
Interaction parameter χ	—	29% vinyl acetate, 150°C, inverse GC, infinite solution		(4, 5)
		Acetaldehyde	0.16	
		Acetic acid	1.12	
		Benzene	−0.02	
		1-Butanol	0.65	
		2-Butanol	0.51	
		Cyclohexane	0.07	

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PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Interaction parameter χ	—	Dioxane	0.45	
		Ethanol	1.28	
		Hexane	0.25	
		Methanol	1.69	
		Octane	0.23	
		2-Propanol	0.93	
		Tetrahydrofuran	0.25	
		m-Xylene	−0.02	
Glass transition temperature	K	30% vinyl acetate, $M_n = 27{,}000\ \mathrm{g\ mol^{-1}}$, $M_w = 110{,}000\ \mathrm{g\ mol^{-1}}$	231	(3)
		40% vinyl acetate, $M_n = 25{,}000\ \mathrm{g\ mol^{-1}}$, $M_w = 130{,}000\ \mathrm{g\ mol^{-1}}$	235	
Melting point	K	30% vinyl acetate, $M_n = 27{,}000\ \mathrm{g\ mol^{-1}}$, $M_w = 110{,}000\ \mathrm{g\ mol^{-1}}$	345	(3)
		40% vinyl acetate, $M_n = 25{,}000\ \mathrm{g\ mol^{-1}}$, $M_w = 130{,}000\ \mathrm{g\ mol^{-1}}$	318	
Brittleness temperature	K	ASTM D746		(2)
		9% vinyl acetate, melt index = 2.2 g/10 min	<197	
		9% vinyl acetate, melt index = 9.8 g/10 min	<197	
		15% vinyl acetate, melt index = 8.2 g/10 min	<197	
		15% vinyl acetate, melt index = 30 g/10 min	<197	
		18% vinyl acetate, melt index = 1.5 g/10 min	<197	
		18% vinyl acetate, melt index = 30 g/10 min	<197	
		19% vinyl acetate, melt index = 0.45 g/10 min	<197	
		19% vinyl acetate, melt index = 30 g/10 min	<197	
		28% vinyl acetate, melt index = 3.1 g/10 min	<197	
Vicat softening temperature	K	ASTM D1525, ring and ball method		(2)
		9% vinyl acetate, melt index = 2.2 g/10 min	356	
		9% vinyl acetate, melt index = 9.8 g/10 min	348	
		15% vinyl acetate, melt index = 8.2 g/10 min	339	
		15% vinyl acetate, melt index = 30 g/10 min	334	
		18% vinyl acetate, melt index = 1.5 g/10 min	334	
		18% vinyl acetate, melt index = 30 g/10 min	327	
		19% vinyl acetate, melt index = 0.45 g/10 min	335	
		19% vinyl acetate, melt index = 30 g/10 min	331	
		28% vinyl acetate, melt index = 3.1 g/10 min	322	
Tensile strength at break	MPa	ASTM D638		(2)
		9% vinyl acetate, melt index = 2.2 g/10 min	13.9	
		9% vinyl acetate, melt index = 9.8 g/10 min	11.7	
		15% vinyl acetate, melt index = 8.2 g/10 min	12.8	
		15% vinyl acetate, melt index = 30 g/10 min	10.4	
		18% vinyl acetate, melt index = 1.5 g/10 min	13.5	

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PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Tensile strength at break	MPa	18% vinyl acetate, melt index = 30 g/10 min	9.0	
		19% vinyl acetate, melt index = 0.45 g/10 min	19.3	
		19% vinyl acetate, melt index = 30 g/10 min	8.1	
		28% vinyl acetate, melt index = 3.1 g/10 min	15.2	
Elongation at break	%	ASTM D638		(2)
		9% vinyl acetate, melt index = 2.2 g/10 min	740	
		9% vinyl acetate, melt index = 9.8 g/10 min	675	
		15% vinyl acetate, melt index = 8.2 g/10 min	730	
		15% vinyl acetate, melt index = 30 g/10 min	750	
		18% vinyl acetate, melt index = 1.5 g/10 min	850	
		18% vinyl acetate, melt index = 30 g/10 min	700	
		19% vinyl acetate, melt index = 0.45 g/10 min	740	
		19% vinyl acetate, melt index = 30 g/10 min	680	
		28% vinyl acetate, melt index = 3.1 g/10 min	750	
1% Secant modulus	MPa	ASTM D638		(2)
		9% vinyl acetate, melt index = 2.2 g/10 min	75.9	
		9% vinyl acetate, melt index = 9.8 g/10 min	93.1	
		19% vinyl acetate, melt index = 0.45 g/10 min	33.1	
		19% vinyl acetate, melt index = 30 g/10 min	29.7	
		28% vinyl acetate, melt index = 3.1 g/10 min	18.6	
Dart drop impact	F_{50} g^{-3}	ASTM D1709		(2)
		9% vinyl acetate, melt index = 2.2 g/10 min	300	
		9% vinyl acetate, melt index = 9.8 g/10 min	305	
		15% vinyl acetate, melt index = 8.2 g/10 min	310	
		18% vinyl acetate, melt index = 1.5 g/10 min	>600	
Flexural modulus	MPa	ASTM D790, no composition given	53.1	(1)
Hardness	Shore D/A values	ASTM D2240		(2)
		9% vinyl acetate, , melt index = 2.2 g/10 min	93 (A)	
		9% vinyl acetate, melt index = 9.8 g/10 min	34 (D)	
		15% vinyl acetate, melt index = 30 g/10 min	30 (D)	
		18% vinyl acetate, melt index = 1.5 g/10 min	42 (D)	
		18% vinyl acetate, melt index = 30 g/10 min	30 (D)	
		19% vinyl acetate, melt index = 30 g/10 min	88 (A)	
		28% vinyl acetate, melt index = 3.1 g/10 min	78 (A)	
Dielectric strength	V mil^{-1}	ASTM D149, no composition given, 0.31-cm thick specimen	620–760	(1)
Water absorption	%	ASTM D570, no composition given, 24 h	0.005–0.13	(1)

* The melt index values were obtained with ASTM D1238.

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Ethylene-vinyl alcohol copolymer

PING XU

ACRONYMS, TRADE NAMES EVA, Clarene® (Colortech); Eval® (Eval); GL®; Levasint® (Bayer)

CLASS Chemical copolymers

STRUCTURE $[-CH_2-CH_2-]_m-[-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-]_n$

MAJOR APPLICATIONS Coextrusion, film lamination, coatings, and food packaging.

PROPERTIES OF SPECIAL INTEREST Superior barrier properties to gases, fragrances, solvents, etc.

PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Linear thermal expansion coefficient	K^{-1}	32 mol% vinyl alcohol, melt index = 3.8 g/10 min	11×10^{-5}	(1)
		38 mol% vinyl alcohol, melt index = 3.8 g/10 min	12×10^{-5}	
		44 mol% vinyl alcohol, melt index = 13.0 g/10 min	13×10^{-5}	
Density	$g\ cm^{-3}$	ASTM D1505		(1)
		27 mol% vinyl alcohol, melt index = 3.0 g/10 min	1.20	
		32 mol% vinyl alcohol, melt index = 3.8 g/10 min	1.19	
		38 mol% vinyl alcohol, melt index = 3.8 g/10 min	1.17	
		44 mol% vinyl alcohol, melt index = 13.0 g/10 min	1.14	
Interaction parameter χ	–	No composition given, 20°C, water	1.2–1.8	(2)
Heat of fusion	$J\ g^{-1}$	32 mol% vinyl alcohol, melt index = 3.8 g/10 min	81.9	(1)
		38 mol% vinyl alcohol, melt index = 3.8 g/10 min	81.1	
		44 mol% vinyl alcohol, melt index = 13.0 g/10 min	79.8	
Heat of combustion	$J\ g^{-1}$	32 mol% vinyl alcohol, melt index = 3.8 g/10 min	30,037	(1)
		38 mol% vinyl alcohol, melt index = 3.8 g/10 min	31,200	

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PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Heat of combustion	$J\,g^{-1}$	44 mol% vinyl alcohol, melt index = 13.0 g/10 min	32,366	
Glass transition temperature	K	Dynamic viscoelasticity		(1)
		27 mol% vinyl alcohol, melt index = 3.0 g/10 min	345	
		32 mol% vinyl alcohol, melt index = 3.8 g/10 min	342	
		38 mol% vinyl alcohol, melt index = 3.8 g/10 min	335	
		44 mol% vinyl alcohol, melt index = 13.0 g/10 min	328	
Melting point	K	DSC		(1)
		27 mol% vinyl alcohol, melt index = 3.0 g/10 min	464	
		32 mol% vinyl alcohol, melt index = 3.8 g/10 min	454	
		38 mol% vinyl alcohol, melt index = 3.8 g/10 min	448	
		44 mol% vinyl alcohol, melt index = 13.0 g/10 min	437	
Tensile modulus	MPa	ASTM D638		(1)
		27 mol% vinyl alcohol, melt index = 3.0 g/10 min	3,138	
		32 mol% vinyl alcohol, melt index = 3.8 g/10 min	2,648	
		38 mol% vinyl alcohol, melt index = 3.8 g/10 min	2,352	
		44 mol% vinyl alcohol, melt index = 13.0 g/10 min	2,062	
Tensile strength at break	MPa	ASTM D638		(1)
		27 mol% vinyl alcohol, melt index = 3.0 g/10 min	71.6	
		32 mol% vinyl alcohol, melt index = 3.8 g/10 min	71.6	
		38 mol% vinyl alcohol, melt index = 3.8 g/10 min	46.1	
		44 mol% vinyl alcohol, melt index = 13.0 g/10 min	51.0	
Elongation at break	%	ASTM D638		(1)
		27 mol% vinyl alcohol, melt index = 3.0 g/10 min	200	
		32 mol% vinyl alcohol, melt index = 3.8 g/10 min	230	

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PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Elongation at break	%	38 mol% vinyl alcohol, melt index = 3.8 g/10 min	280	
		44 mol% vinyl alcohol, melt index = 13.0 g/10 min	380	
Izod impact strength	$J\,m^{-1}$	ASTM D255, notched		(1)
		27 mol% vinyl alcohol, melt index = 3.0 g/10 min	58.7	
		32 mol% vinyl alcohol, melt index = 3.8 g/10 min	90.7	
		38 mol% vinyl alcohol, melt index = 3.8 g/10 min	64.1	
		44 mol% vinyl alcohol, melt index = 13.0 g/10 min	53.4	
Rockwell hardness	—	ASTM D785		(1)
		27 mol% vinyl alcohol, melt index = 3.0 g/10 min	104	
		32 mol% vinyl alcohol, melt index = 3.8 g/10 min	100	
		38 mol% vinyl alcohol, melt index = 3.8 g/10 min	93	
		44 mol% vinyl alcohol, melt index = 13.0 g/10 min	88	
Taber abrasion	mg	ASTM D1175, 1,000 times		(1)
		32 mol% vinyl alcohol, melt index = 3.8 g/10 min	1.2	
		38 mol% vinyl alcohol, melt index = 3.8 g/10 min	2.0	
		44 mol% vinyl alcohol, melt index = 13.0 g/10 min	2.2	
Bending strength	MPa	ASTM D790		(1)
		27 mol% vinyl alcohol, melt index = 3.0 g/10 min	149	
		32 mol% vinyl alcohol, melt index = 3.8 g/10 min	128	
		38 mol% vinyl alcohol, melt index = 3.8 g/10 min	108	
Surface resistivity	ohm	Various films	$1.9\text{–}2.7 \times 10^{15}$	(1)
Volume resistivity	ohm cm	Various films	$0.47\text{–}1.2 \times 10^{13}$	(1)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	32 mol% vinyl alcohol, melt index = 3.8 g/10 min	0.35	(1)
		44 mol% vinyl alcohol, melt index = 13.0 g/10 min	0.36	

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PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Water permeability	cm^3 25 μm $(m^2 \text{ day atm})^{-1}$	Eval films, 40°C	21.7–124	(3)
Oxygen permeability	cm^3 25 μm $(m^2 \text{ day atm})^{-1}$	Eval films, 23°C	0.095–1.8	(3)
Water absorption	%	24 h, Eval® F resins	0.19–7.7	(4)

* The melt index values were obtained with ASTM D1238.

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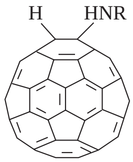
Fullerene-containing polymers

WARREN T. FORD AND ALANTA LARY

CLASS Cage structure polymers

STRUCTURES



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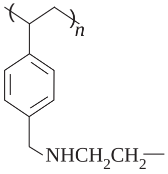

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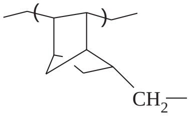

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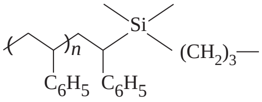

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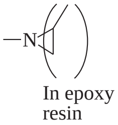
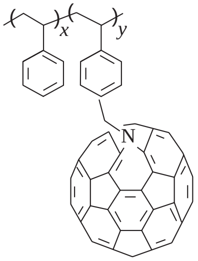


R4



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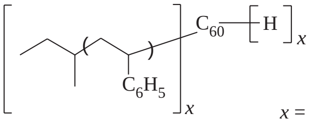

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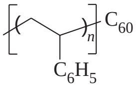

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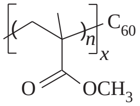

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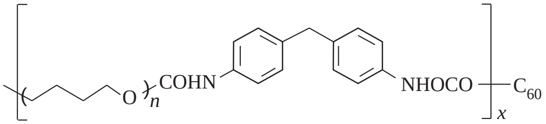

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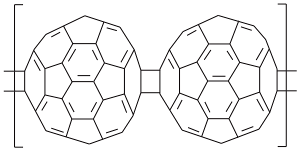

7

MAJOR APPLICATIONS Electrical and optical materials, crosslinking of elastomers, and low-friction films, none of which are commercial.

PROPERTIES OF SPECIAL INTEREST Electrical conductivity, photoconductivity, and nonlinear optical activity.

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STRUCTURE	C_{60} (wt %)	M_n (g mol^{-1})	M_w/M_n	SOLVENTS	ANALYSES	REFERENCE
1 (R1)	18	20,000	NR	Toluene, CS_2	^{13}C MAS NMR, IR, UV-vis, TGA	(1)
1 (R2)	2.6	20,000	NR	Toluene, THF, heptane	IR	(2)
1 (R3)	4.3	12,100	1.24	Toluene	UV, ^{13}C NMR, DSC	(3)
2	29	12,300	3.1	$CHCl_3$, THF, C_6H_5Cl	UV-vis, IR, ^1H NMR, DSC, TGA	(4)
3	0.5	146,000	1.06	THF, toluene	Light scattering	(5)
3	0.9	82,000	Bimodal	–	–	–
3	14	5,300, 3,000	Bimodal	THF	SANS $R_g = 19.6$ Å	(6)
4	5	14,500	1.12	Toluene, THF	DSC, photoconductivity	(7)
4	2.2	12,900	1.8	Benzene, 1,4-dioxane	–	(8)
4	14	38,000 (M_w)	NR	$CHCl_3$, toluene, *o*-$C_6H_4Cl_2$	–	(9)
5	7.7	4,200	1.8	–	^{13}C NMR, DSC, TGA	(10)
5	1.2	23,000	1.4	–	GPC (UV, RI, LS, viscometry)	(11)
6	NR	18,000	1.45	THF : DMF (3 : 1)	IR, DSC, TMA	(12)
1 (R4)	19	–	–	Insoluble	TGA, coeff. friction	(13)
Photo polymer of C_{60} (7)	100	$(720)_n$, $n = 1$–21	–	Insoluble	MS, SEM, IR, Raman, XRD, LDMS	(14) (15)
Pressure polymer of C_{60} (7)	100	$(720)_n$	–	Insoluble	XRD, Raman, IR, ^{13}C MAS NMR	(16)
Single-walled carbon nanotubes			1.38 nm diameter × > 1 μm long in ropes of 100–500 tubes		XRD, SEM, TEM, single-rope $\rho < 10^{-4}$ ohm cm at 300 K	(17)
Multiwalled carbon nanotubes			Average 7 nm diameter × 2 μm long		TEM, tensile modulus 1.8×10^6 MPa	(18)

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Gelatin

W. BROOKE ZHAO

CLASS Polypeptides and proteins

STRUCTURE $-\!\!\left(\text{Glycine}-X-Y\right)\!\!-_n$
X and Y are frequently proline and hydroxy-proline, respectively.

MAJOR APPLICATIONS Food, pharmaceutical, photographic, and biodegradable packaging materials.

PROPERTIES OF SPECIAL INTEREST The ability of gelation by temperature changes. Relatively low cost. The polypeptide backbone is biodegradable. Manufacturing from waste.

PREPARATIVE TECHNIQUES Thermal denaturation and physical and chemical degradation of collagen.

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Amino acid composition	Numbers per 1,000 residues		Type A	Type B	(1)
		Alaine	112	117	
		Arginine	49	48	
		Asparagine	16	0	
		Aspartic acid	29	46	
		Cysteine	—	0	
		Glutamic acid	48	72	
		Glutamine	48	0	
		Glycine	330	335	
		Histidine	4	4.2	
		Hydroxyproline	91	93	
		Hydroxylysine	6.4	4.3	
		Isoleucine	10	11	
		Leucine	24	24.3	
		Lysine	27	28	
		Methionine	3.6	3.9	
		Phenylalanine	14	14	
		Proline	132	124	
		Serine	35	33	
		Threonine	18	18	
		Tryptophan	—	—	
		Tyrosine	2.6	1.2	
		Valine	26	22	

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	Alpha		9.65×10^4	(1)
		Beta		1.93×10^5	
		Gamma		2.89×10^5	
		Limed-ossein		2.2×10^5	
		Weight-average		$(1 - >5) \times 10^5$	
		Number-average		$(5\text{–}15) \times 10^4$	
Gel rigidity	Bloom	Depending on source and extracting conditions		75–330	(1)
Density	$g\,cm^{-3}$	–		1.35	(2)
IR (characteristic absorption frequencies)	cm^{-1}	–C=O stretching		1,650	(3)
		–NH stretching		3,300	
Common solvents	Water (warm), acetic acid, trifluro-ethanol, formamide, ethylene glycol, glycerol, dimethyl sulfoxide				(1)
Common nonsolvents	Ethanol, acetone, tetrahydrafuran				(1)
Isoionic pH	–	Type A		4.8–5.2	(1)
		Type B		7–9	
pK_a of the ionizable side groups of gelatin	–	Anionic amino acid	Conc. ($mmol\,g^{-1}$)		(4)
		Aspartic acid	0.50, 0.32	4-4.5	
		Glutamic acid	0.78, 0.52	4.5	
		Tyrosine	0.011–0.044	10	
		α-COOH	0.011	3.6	
		Cationic amino acid			
		Lysine	0.30	10–10.4	
		Hydroxylysine	0.054	9.5	
		Arginine	0.53	>12	
		Histidine	0.044	6.5–7	
		α-NH_2	0.011	7.8	
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$; a = None	Calf skin gelatin		$K = 1.66 \times 10^{-5}$; $a = 0.885$	(5)
		Pig skin		$K = 1.10 \times 10^{-4}$; $a = 0.74$	(6)
Radius of gyration	Å	Alpha		138	(1)
		Beta		215	
		Gamma		257	

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Radius of gyration	Å	Solvent	M_w (ossein gelatin)		(7)
		1.0 M KCNS, 25°C, pH = 5.1	90,000	175	
		0.15 M NaCl, 40°C			
		pH = 5.1	89,000	165	
		pH = 3.1	88,000	175	
			M_w (Type B)		(8)
		0.05 M phosphate	2.7 × 105	302	
		1.0 M KCNS	3.02 × 105	302	
		1.0 M KCNS	3.83 × 105	242	
		1.0 M KCNS	5.96 × 105	280	
		Alcohol–water ratio	M_w (bovine corium extract)		(9)
		2:1 ~ 2.5:1	8.33×10^6	2,410	
		2.5: 1 ~ 3.0:1	7.45×10^5	444	
		2.5: 1 ~ 3.0:1	3.45×10^5	314	
		2.5:1 ~ 3.0:1	2.32×10^5	371	
		3.0:1 ~ 3.5:1	2.02×10^5	345	
			$M_w \times 10^{-5}$		(10)
		0.2 M KCl	3.3 (acid-precusor)	452	
		0.2 M KCl	3.3 (alkali-precusor)	447	
		Rousselot gelatin, photographic grade, $M_w = 1.9 \times 10^5$, $M_w/M_n = 2.3$		350 ± 40	(11)
Radius of gyration of the cross-section R_c	Å	Rousselot gelatin, photographic grade, $M_w = 1.9 \times 10^5$, $M_w/M_n = 2.3$		3.2 ± 1	(11)
Root-mean-square end-to-end distance $(\overline{r^2})^{1/2}$	Å	Solvent	M_w (Type B gelatin)		(8)
		0.05 M phosphate	2.7×10^5	740	
		1.0 M KCNS	3.02×10^5	740	
		1.0 M KCNS	3.83×10^5	590	
		1.0 M KCNS	5.96×10^5	685	
Expansion coefficient α	–	Solvent	M_w (Type B gelatin)		(8)
		1.0 M KCNS	3.83×10^5	1.25	
		1.0 M KCNS	5.96×10^5	1.25	
Universal constant Φ	–	Solvent	M_w (Type B gelatin)		(8)
		1.0 M KCNS	3.83×10^5	1.29×10^{21}	
		1.0 M KCNS	5.96×10^5	1.63×10^{21}	

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Second virial coefficient A_2	mol cm^3 g^{-2}	Solvent	M_w (ossein gelatin)		(7)
		1.0 M KCNS, 25°C pH = 5.1	9×10^4	2.6×10^{-4}	
		0.15 M Nalco, 40°C			
		pH = 5.1	8.9×10^4	2.9×10^{-4}	
		pH = 3.1	8.8×10^4	6.0×10^{-4}	
			M_w (Type B)		(8)
		0.05 M phosphate	2.7×10^5	2.4×10^{-4}	
		1.0 M KCNS	3.02×10^5	2.6×10^{-4}	
		1.0 M KCNS	3.83×10^5	3.3×10^{-4}	
		1.0 M KCNS	5.96×10^5	2.4×10^{-4}	
		Rousselot gelatin, photographic grade, $M_w = 1.9 \times 10^5$, $M_w/M_n = 2.3$		$(3 \pm 1) \times 10^{-4}$	(11)
Persistence length l	Å	Rousselot gelatin, photographic grade, $M_w = 1.9 \times 10^5$, $M_w/M_n = 2.3$		20 ± 3	(11)
Mass per unit length	g mol^{-1} Å^{-1}	Rousselot gelatin, photographic grade, $M_w = 1.9 \times 10^5$, $M_w/M_n = 2.3$		28 ± 8	(11)
Screen length ξ	Å	Rousselot gelatin, photographic grade, $M_w = 1.9 \times 10^5$, $M_w/M_n = 2.3$			(11)
		1%		70 ± 10	
		2%		51 ± 5	
		5%		35 ± 3	
Hydrodynamic screen length ξ_h	Å	Quasi-elastic light scattering, dilute solution, Rousselot gelatin, photographic grade, $M_w = 1.9 \times 10^5$, $M_w/M_n = 2.3$, concentration ranges from 5 to 15%		25–100	(12)
Sizes of inhomogeneities a	Å	Rousselot gelatin, photographic grade, $M_w = 1.9 \times 10^5$, $M_w/M_n = 2.3$			(11)
		1%		—	
		2%		220	
		5%		135	
z-average self-diffusion coefficient $\langle D_0 \rangle_z$	cm^2 s^{-1}	Quasi-elastic light scattering, dilute solution Rousselot gelatin, photographic grade, $M_w = 1.9 \times 10^5$, $M_w/M_n = 2.3$		2×10^{-7} (fast-mode) 3.5×10^{-8} (slow-mode)	(12)
Hydrodynamic radius R_h	Å	Quasi-elastic light scattering, Rousselot gelatin, photographic grade, $M_w = 1.9 \times 10^5$, $M_w/M_n = 2.3$			(12)
		In dilute solution		220	
		In semi-dilute solution		210	

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Flory-Huggins interaction parameter χ	–	Type A gelatin			(13)
		283.15 K		0.497–0.498	
		293.15 K		0.497	
Self-diffusion coefficient D	$cm^2\ s^{-1}$	Gelatin, quasi-elastic neutron scattering	Volume fraction		(14)
			0.031	1.36×10^7	
			0.063	1.01×10^7	
			0.129	7.1×10^6	
			0.199	6.1×10^6	
			0.274	5.3×10^6	
			0.353	4.9×10^6	
Collective self-diffusion coefficient D_{coll}	$cm^2\ s^{-1}$	Gelatin, quasi-elastic neutron scattering	Volume fraction		(14)
			0.031	4.8×10^6	
			0.063	5.2×10^6	
			0.129	5.2×10^6	
			0.199	5.4×10^6	
			0.274	5.1×10^6	
			0.353	4.8×10^6	
Single-particle self-diffusion coefficient $D_{s\text{-}p}$	$cm^2\ s^{-1}$	Gelatin, quasi-elastic neutron scattering	Volume fraction		(14)
			0.031	8.8×10^6	
			0.063	4.9×10^6	
			0.129	1.9×10^6	
			0.199	7.0×10^5	
			0.274	2.0×10^5	
			0.353	1.0×10^5	
Residence time τ_0	s	Gelatin, quasi-elastic neutron scattering	Volume fraction		(14)
			0.031	2.0	
			0.063	2.7	
			0.129	9.8	
			0.199	22	
			0.274	66	
			0.353	165	
Specific optical rotation $[\alpha]$	Degree	Alpha		−137	(1)
		Beta		−137	
		Gamma		−137	
		Limed-ossein		−137	
Refractive index	–	Dry, $\lambda = 546.1$ nm		1.54	(15)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Refractive increment dn/dc	—	$\lambda = 300$ nm	0.187	(16)
		$\lambda = 436$ nm		
		Ossein gelatin		(7)
		H_2O, 25°C	0.194	
		0.1 M NaCl, 25°C	0.1925	
		1.0 M NaCl, 25°C	0.186	
		1.0 M KCNS, 25°C	0.185	
		2.0 M KCNS, 25°C	0.173	
		Bovine corium extract		
		H_2O, 40°C	0.192	(9)
		0.25 M NaCl, 40°C	0.192	(9)
		0.10 M KCl, 40°C	0.192	(9)
		0.25 M KCl, 40°C	0.192	(9)
		1.0 M KCl, 40°C	0.176	(17)
		Type B gelatin		(8)
		1.0 M KCNS, 30°C	0.172	
		0.1 M KH_2PO_4, 30°C	0.172	
		0.1 M K_2HPO_4, 30°C	0.172	
		$\lambda = 632.8$ nm, Rousselot gelatin, photographic grade, $M_w = 1.9 \times 10^5$, $M_w/M_n = 2.3$	0.18	(11)
Glass transition temperature T_g	K	Dilatometry	368	(18)
		Viscoelastic	393	
		Viscoelastic	463 (calculated)	
		Viscoelastic	453	
		Thermomechanical	473	
		DTA, viscoelastic	448 ± 10 (uncross-linked)	
		DTA, viscoelastic	469 ± 3 (cross-linked)	
Melting temperature T_m	K	Dilatometry	418	(18)
		DTA, X-Ray	491	
		Viscoelastic	493	
		DTA, TGA	503 (calculated)	
		DSC	503	
		DTA, X-Ray	503	
Activation energy of hydrolysis	$kJ\,mol^{-1}$	pH		(19)
		3.05	107.2	
		3.60	107.2	
		4.75	72.2	
		7.10	72.2	
		8.50	72.2	
		9.35	72.2	
		9.85	108.8	

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Contact angle of water	Degrees	15% aqueous gelatin gel, 20°C		75	(20)
		Gelatin hydrogel			(21)
		Air-equilibrated surface		110	
		Fresh-cut wet surface		36	
		Gelatin film, Langmuir-Bloggett process			(22)
		Surface in contact with air		110	
		Surface in contact with benzene		90	
Tensile strength	MPa	Type B, uniaxially oriented in water, ν_2 at stretching = 0.2–0.25	Stretching ratio (%)		(23)
			0	25.61	
			65	41.57	
			120	63.39	
			145	84.84	
			180	27.87(⊥)*	
			87	74.94	
		Biaxial Type A, uniaxially oriented in water, ν_2 at stretching = 0.2–0.25	0	28.36	
			75	54.48	
			125	80.88	
			155	109.19	
			190	139.80	
			110	60.46(⊥)*	
			160	44.31(⊥)*	
		Biaxial	50	50.68	
			90	104.47	
			110	128.37	
Tensile modulus	MPa	Type B, uniaxially oriented in water, ν_2 at stretching = 0.2–0.25	Stretching ratio (%)		(23)
			0	473	
			65	690	
			120	790	
			145	1300	
			180	930(⊥)*	
			87	1345	
		Biaxial Type A, uniaxially oriented in water, ν_2 at stretching = 0.2–0.25	0	631	
			75	890	
			125	1090	
			155	1240	
			190	1690	
			110	1100(⊥)*	
			160	1040(⊥)*	
		Biaxial	50	1090	
			90	1200	
			110	1570	

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Elongation at break	%	Type B, uniaxially oriented in water, ν_2 at stretching = 0.2–0.25	Stretching ratio (%)		(23)
			0	7.7	
			65	8.3	
			120	12.3	
			145	8.3	
			180	3.6(⊥)*	
			87	15.5	
		Biaxial Type A, uniaxially oriented in water ν_2 at stretching = 0.2–0.25	0	6.7	
			75	11.4	
			125	14.9	
			155	21.6	
			190	22.5	
			110	7.7(⊥)*	
			160	5.5(⊥)*	
		Biaxial	50	5.86	
			90	14.5	
			110	18.4	
Toughness	MPa	Type B, uniaxially oriented in water, ν_2 at stretching = 0.2–0.25	Stretching ratio (%)		(23)
			0	1.24	
			65	2.31	
			120	5.00	
			145	4.05	
			180	0.60(⊥)*	
			87	8.93	
		Biaxial Type A, uniaxially oriented in water, ν_2 at stretching = 0.2–0.25	0	1.26	
			75	4.15	
			125	8.42	
			155	17.13	
			190	23.85	
			110	3.00(⊥)*	
			160	1.45(⊥)*	
		Biaxial	50	1.86	
			90	9.51	
			110	17.56	

*Property measured at the direction perpendicular to the orientation direction.

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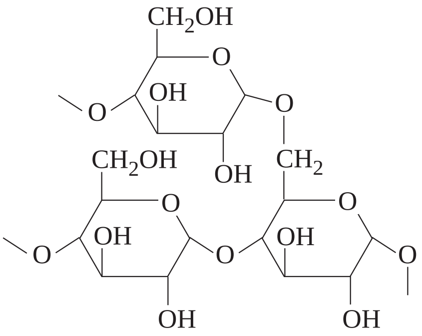
Glycogen

RACHEL MANSENCAL

CLASS Carbohydrate polymers; polysaccharides.

STRUCTURE Branched glucan. α-D-glucopyranosyl units joined by α-D-$(1 \rightarrow 4)$ glycosidic linkages.[1–2]



FUNCTIONS Biological function restricted to source of energy. Principal food-reserve materials in animals. Found in cells of vertebrates and invertebrates. No commercial use.[1–2]

EXTRACTION Extraction with hot concentrated alkali. But extensive degradation. Milder extraction with cold trichloracetic acid solution, dimethyl sulfoxide, or water-phenol mixtures.[1–6]

PURIFICATION After extraction, redissolution in distilled water; low speed centrifugation (100 g); precipitation with excess ethanol; high speed centrifugation (1,500 g).[2]

PROPERTIES OF SPECIAL INTEREST Amorphous polymer; very high molecular weight; polydisperse; highly soluble; very good hydrodynamic behavior.[1–2]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight	$g\,mol^{-1}$	Rabbit liver	2.7×10^8	–
Average degree of polymerization	–	–	1.7×10^6	(1–2)
Average chain length	–	Depending on the source of the glycogen and the method used	6–21	(1–2)
Average interior chain length	–	Depending on the source of the glycogen and the method used	2–5	(1–2)
Morphology	–	α-particle $\approx$ 100 β-particles β-particle diameter = 25 nm	–	(2)

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Action of enzymes on glycogen[2]

Enzyme	Glucosidic bond attacked	Source
Phosphorylase	$(1 \rightarrow 4)$-α	Plants, microbes, mammals
Amylo-1,6-glucosidase	$(1 \rightarrow 4)$-α	Yeast, mammals
	$(1 \rightarrow 6)$-α	
Pullulanase	$(1 \rightarrow 6)$-α	*Aerobacter aerogenes*
Glucoamylase	$(1 \rightarrow 4)$-α	Microbes
Isoamylase	$(1 \rightarrow 6)$-α	*Cytophaga pseudomonas*
β-Amylase	$(1 \rightarrow 4)$-α	Sweet potato, cereals

Weight mean sedimentation coefficients of glycogen fraction[2]

Fraction number	$s^0_{20,\mathrm{w}}$ at boundary (S)	Absolute range (S)	$\bar{s}_\mathrm{w}$ (S)
20	0	0–85	26
19	46	0–181	85
18	114	40–292	175
17	225	150–419	291
16	353	278–561	422
15	495	420–717	570
14	651	576–884	732
13	818	743–1,061	904
12	915	920–1,249	1,087
11	1,182	1,107–1,444	1,278
10	1,378	1,303–1,648	1,478
9	1,581	1,507–1,858	1,658
8	1,792	1,717–2,074	1,898
7	2,008	1,933–2,298	2,117
6	2,231	2,156–2,531	2,346
5	2,464	2,389–2,781	2,588
4	2,714	2,639–3,064	2,855
3	2,998	2,923–3,428	3,178
2	3,361	3,286–4,020	3,647
1	3,953	3,878–7,077	4,335
0	7,010	—	—

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Z-average standard diffusion coefficients of glycogen fractions[2]

Fraction number	$\overline{D}z$ (10^{-8} cm^2 s^{-1})
20	2.56 ± 0.02
19	2.7 ± 0.4
18	4.3 ± 0.3
17	5.90 ± 0.07
16	5.8 ± 0.1
15	5.1 ± 0.1
14	4.3 ± 0.1
13	3.6 ± 0.1
12	3.4 ± 0.1
11	3.01 ± 0.05
10	2.74 ± 0.07
9	2.73 ± 0.04
8	2.59 ± 0.04
7	2.42 ± 0.04
6	2.6 ± 0.2
5	2.27 ± 0.06
4	2.42 ± 0.06
3	2.21 ± 0.04
2	2.18 ± 0.02
1	2.5 ± 0.1

Hydrodynamic parameters for glycogen subfractions[2,7]

Fraction number	Average molecular weight ($\times 10^{-6}$)	Scheraga-Mandelkern function β ($\times 10^{-6}$)	Viscosity (ml g^{-1})	Frictional ratio (f/f_{min})
20	6	0.61	14	7.1
19	20	0.71	9	5.0
18	26	1.26	6.5	2.6
17	32	1.75	6.0	1.8
1–16	48–1600	2.06 ± 0.17	6.7 ± 0.4	1.7 ± 0.1

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Hydridopolysilazane

DONNA M. NARSAVAGE-HEALD

ACRONYM HPZ

CLASS Polysilazanes

EMPIRICAL FORMULA $(SiH)_{39.7}(Me_3Si)_{24.2}(NH)_{37.3}(N)_{22.6}$

MAJOR APPLICATION Composites

PROPERTIES OF SPECIAL INTEREST Preceramic polymer; melt-spinnable polymer; produces a ceramic fiber upon pyrolysis.

PREPARATIVE TECHNIQUE Condensation (step) polymerization: Exothermic reaction; temperature rises to 75°C. Mixture is heated to 150°C and eventually to 200–230°C. Reaction of trichlorosilane with hexamethyldisilazane (1 :≥ 3 mol ratio) in Ar purged flask at room temperature.[1]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight	$g\ mol^{-1}$	GPC data	$M_n = 3{,}800$ $M_w = 15{,}100$ $M_z = 38{,}000$	(1)
NMR	ppm	^1H	0.2, broad, SiMe 1.0, broad, NH 4.8, broad, SiH	(1)
Glass transition temperature	K	TMA	368	(1)
Melt viscosity	P	Determined using a viscometer in a glove box; at 503 K	100	(1)
Pyrolyzability, nature of product	–	$3°C\ min^{-1}$ to 1,200°C under high purity N_2	Silicon carbonitride	(1)
Pyrolyzability, amount of product	–	TGA, N_2 flow	74%	(1)
Pyrolyzability, impurities remaining	–	$3°C\ min^{-1}$ to 1,200°C under high purity N_2	~5 wt% carbon, 2.2 wt% oxygen	(1)
Decomposition temperature	K	TGA	563	(1)
Fiber spinning	–	Inert atmosphere	Fibers ≤ 15–20 μm obtained	–
Important patents		U.S. Patent 4,535,007 U.S. Patent 4,543,344		(2) (3)

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3. Cannady, J. P. *U.S. Patent* 4,543,344 (24 September 1985).

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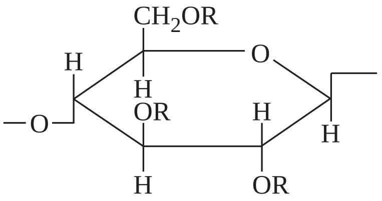
Hydroxypropylcellulose

YONG YANG

ACRONYM HPC

CLASS Carbohydrate polymers

STRUCTURE



(R is $CH_2CH(OR')CH_3$ or H, R′ is R or H)

MAJOR APPLICATIONS Paints, coatings, inks, adhesives, cosmetics, papers, pharmaceuticals, encapsulation.

PROPERTIES OF SPECIAL INTEREST Water and alcohol soluble.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	Molar substitution (MS) = 3.0	336	–
Preparation		Cellulose + NaOH → Na-cellulose (alkali cellulose) Na-cellulose + Propylene oxide → Hydroxypropylcellulose		(1)
Density	$g\,cm^{-3}$	Water cast film	1.17	(2)
^{13}C NMR	–	–	–	(3)
IR (characteristic absorption frequencies)	cm^{-1}	Assignment		(2, 4)
		(OH) side chain stretching	3,450	
		(OH) ring stretching	3,440	
		(CH_3) asymmetric stretching	2,965	
		(CH_2) asymmetric stretching	2,930	
		(CH_2) symmetric stretching	2,900	
		(CH_3) symmetric stretching and CH ring stretching	2,870	
		(CH_3) asymmetric bending deformation	1,455	
		(OH + CH) side chain bending deformation	1,425	
		(OH + CH) ring bending deformation	1,410	
		(CH_3) symmetric bending deformation	1,373	
		(OH + CH) ring bending deformation	1,324	
		(OH + CH) side chain bending deformation	1,300	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
IR (characteristic absorption frequencies)	cm^{-1}	Assignment (CH) ring bending deformation	1,265	
		(C–O–C) ring asymmetric stretching	1,150	
		(C–O) side chain stretching	1,126	
		(C–O–C) ring asymmetric stretching	1,120	
		(C–O–C) side chain asymmetric stretching	1,085	
		(C–O) ring stretching	1,055	
		(C–O–C) ether bridge asymmetric stretching	1,045	
Solvents	Acetic acid*, acetone*, acetonitrile*, benzene:water (1:1), chloroform, cyclohexanone, dichloroacetice acid*, dichloromethane*, *N,N*-dimethylacetamide*, dimethylformamide*, dimethylsulfoxide*, dioxane*, ethanol*, ethylene glycol monomethyl ether*, formamide*, formic acid*, 2-hydroxyethyl methacrylate*, isopropanol*, methanol*, 2-methoxyethanol*, methyl ether ketone*, morphloline*, 2,2′-oxydiethanol*, 1-pentanol*, phenol*, 1,2-propanediol*, 1-propanol*, propylene glycol, pyridine*, tetrahydrofuran, triethyl phosphate*, trifluoroacetic acid*, trimethyl phosphate*, water*			(5–10)
Nonsolvents	Aliphatic hydrocarbons, benzene, carbon tetrachloride, methyl chloroform, toluene, trichloroethylene			(5–10)

*Forms liquid crystalline mesophase

Solubility parameter (δ) and interaction parameter (χ) at infinite dilution*[11, 12]

Solvent	δ ($MPa^{1/2}$)	χ
Acetic acid	25.6	−2.28
Acetic anhydride	20.8	−1.65
Acetone	19.3	0.38
1-Butanol	24	0.26
n-Butyl acetate	17.2	0.14
Cyclohexane	16.3	0.96
Cyclohexanol	21.0	2.31
Cyclohexanone	20.1	0.18
N-Decane	18.8	1.83
Dichloromethane	19.8	−0.38
N,N-dimethylformamide	29.3	−0.01
Dimethylsulfoxide	25.8	−0.19
Diethyl ether	15.1	−0.14
1,4-Dioxane	19.3	0.06
Ethanol	26	0.38
N-haptane	14.8	0.10
Methanol	29	0.47
1-Proponal	24	0.26
2-Proponal	24	0.43

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Solvent	δ (MPa$^{1/2}$)	χ
Pyridine	21.0	−0.42
Tetrachloromethane	16.8	0.45
Tetrahydrofuran	18.6	−0.12
Toluene	17.7	0.17
Trichloromethane	18.0	−0.73
Water	47	1.55

*By inverse GC; MS = 4.0; $M_w = 10^5$; 323.4 K.

Unit cell dimension[2]

Lattice	Monomers per unit cell	Chains per unit cell	Cell dimension (Å)		
			a	b	c
Tetragonal	6	2	11.3	11.3	15.0

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Mark-Houwink parameters: *K* and *a*	K = ml g^{-1} a = None	$[\eta] = K'_m$ (DP = Degree of polymerization), ethanol, 25°C	$K'_m = 0.121$ $a = 1.17$	(13)
Chain conformation	—	—	Irregular 3_1 helix	(2)
Degree of crystallinity	%	Water cast film	14.9	(2)
Heat of fusion (of repeat units)	kJ mol^{-1}	Melting point depression due to a diluent	10.6	(2)
Entropy of fusion (of repeat units)	kJ mol^{-1}	Melting point depression due to a diluent	0.021	(2)
Density	g cm^{-3}	Amorphous region, 24°C Crystalline region, MS = 4.0, calculated from crystallographic data	1.088 2.054	(2)
Glass transition temperature	K	Dynamic mechanical property measurement	298	(14)
Melting point	K	MS = 4	481	(2)
Mesomeric transition temperature	K	Isotropic to cholesteric	433–473	(15)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile modulus	MPa	—	414	(16)
		MS = 4.25, H_2O cast	440	(17)
		MS = 4.25, MeOH cast	1240	(17)
		MS = 4.25, DMAc cast	570	(17)
			703	(8)
		MS = 4.0, lightly cross-linked, $\overline{M}_c = 1.23 \times 10^3$ g mol^{-1}	6.2×10^2	(18)
Storage modulus	MPa	288–413 K, 110 Hz	$(2.5–0.3) \times 10^3$	(5)
Loss modulus	MPa	288–413 K, 110 Hz	$(2.6–0.4) \times 10^2$	(5)
Tensile strength	MPa	—	13.8	(16)
		MS = 4.25, H_2O cast	9.3	(17)
		MS = 4.25, MeOH cast	24	(17)
		MS = 4.25, DMAc cast	9	(17)
			16	(19)
		MS = 4.0, lightly cross-linked, $\overline{M}_c = 1.23 \times 10^3$ g mol^{-1}	16	(18)
Maximum extensibility	%	—	50	(20)
		Cross-head speed = 5 mm min^{-1}		(17)
		MS = 4.25, H_2O cast	17.3	
		MS = 4.25, MeOH cast	3.5	
		MS = 4.25, DMAc cast	7.0	
		Cross-head speed = 2.5 mm min^{-1}, MS = 4.0, lightly cross-linked, $\overline{M}_c = 1.23 \times 10^3$ g mol^{-1}	100	(18)
Index of refraction n	—	—	1.48	(2)
Refractive index increment dn/dc	ml g^{-1}	Ethanol, $\lambda = 546$ nm	0.120	(20)
		Water, $\lambda = 436$ nm	0.146	
		Water, $\lambda = 546$ nm	0.143	
		Water, $\lambda = 578$ nm	0.143	
Dielectric constant ε''	—	1,000 Hz, 297 K		(1)
		101.3 kPa, 38% RH	9.07	
		133 Pa, 0% RH	6.71	
Dielectric loss ε''	—	1,000 Hz, 297 K		(1)
		101.3 kPa, 38% RH	0.0706	
		133 Pa, 0% RH	0.0408	
Resistivity	ohm cm^{-1}	297 K, 101.3 kPa, 38% RH	5×10^9	(1)
		133 Pa, 0% RH	9×10^{11}	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Water absorption	%	50% RH, 296 K	4	(1)
		84% RH, 296 K	12	

Supplier	American International Chemical, Inc., 17 Strathmore Road, Natick, Massachusetts 01760, USA Barrington Chemical Corp., 16 School Street, Rye, New York 10580, USA Hercules, Inc., 1313 North Market Street, Wilmington, Delaware 19894, USA

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Kevlar

BRENT D. VIERS

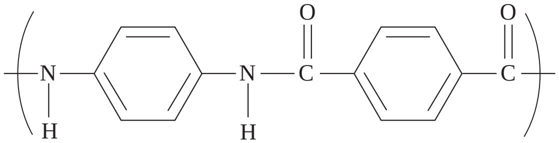
ACRONYM, ALTERNATIVE NAMES PPTA, poly(*p*-phenylene terephthalamide), aramid, aramide, polyaramid, polyaramide

IUPAC NOMENCLATURE Poly(imino-1,4-phenyleneiminocarbonyl-1,4-phenylenecarbonyl)

CAS REGISTRY NUMBER 24938-64-5

CLASS Aromatic polyamides

STRUCTURE



MAJOR APPLICATIONS Cut, heat, and bullet-fragment resistant apparel, brake and transmission friction parts, gaskets, ropes and cables, composites, fiber-optic cables, circuit-board reinforcement, sporting goods, tires, automotive belts and hoses.

MAJOR FORMS Continuous filament yarn, staple, wet and dry pulp floc, cord.

PROPERTIES OF SPECIAL INTEREST High tensile strength at low weight, low elongation to break, high modulus (structural rigidity), low electrical conductivity, high chemical resistance, low thermal shrinkage, high toughness (work-to-break), excellent dimensional stability, high cut resistance, flame resistant, self-extinguishing.

OTHER POLYMER SHOWING THIS SPECIAL PROPERTY Polybenzamide. (See also the entry on *Polybenzamide* in this handbook.)

SUPPLIER Kevlar is a registered trademark of E. I. Dupont de Nemours.

Preparative techniques

PROPERTY	CONDITIONS	VALUE	REFERENCE
Condensation of terephthaloyl chloride and paraphenylene diamine	Interfacial polymerization Low temperature solution condensation		(1)
Direct syntheses	Yamazaki procedure (PBA): Para-aminobenzoic acid (pABA) Pyridine (as acid scavenger) (Py) N-methyl pyrrolidone (NMP) Triphenyl phosphate activator (TPP) Lithium chloride (LiCl) Dry conditions/inert atmosphere	$[pABA] = 0.75\,mol\,l^{-1}$ NMP/Py = 3 (v/v) 3.7% $LiCl_2$ (w/v) [TPP]/[pABA] = 0.6 $T = 115°C$ (higher M_w when TPP added stepwise)	(2)

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PROPERTY	CONDITIONS	VALUE	REFERENCE
Direct syntheses	Yamazaki procedure (PPTA) Terephalic acid (TA) *p*-Phenylene diamine (PPD) NMP, TPP, LiCl	[TA] = [PPD] = 0.125 mol l^{-1} NMP/Py = 1.5 (v/v) [TPP]/[TA] = 2.0 2.7% LiCl, $T = 115°C$	(2)
	Higashi Procedure (PBA): As Yamazaki, with calcium chloride ($CaCl_2$)	[pABA] = 0.27 mol l^{-1} NMP/Py = 5 (v/v) [TPP]/[pABA] = 0.6 1.7% LiCl (w/v); 5.0% $CaCl_2$ (w/v) $T = 115°C$ (Higher M_w when TPP added stepwise)	
	Higashi procedure (PPTA): As Yamazaki, with $CaCl_2$	[TA] = [PPD] = 0.083 mol l^{-1} NMP/Py = 5 (v/v) [TPP]/[TA] = 2.2 1.7% LiCl (w/v); 5.0% $CaCl_2$ (w/v) $T = 115°C$	

Effect of salt in the synthesis of PBA[2]

$LiCl_2$ (% w/v)	$CaCl_2$ (% w/v)	LiCl + $CaCl_2$ (% w/v)	η_{inh} (dl g^{-1})
3.7	0.0	3.7	2.00*
3.7	11.3	15.0	2.15*
0.9	2.8	3.7	0.85*
1.6	4.8	6.4	1.53†
1.4	0.0	1.4	1.82†
6.7	0.0	6.7	2.19†

*[pABA] = 0.75; NMP/Py = 3; [TPP]/[pABA] = 0.6.
†[pABA] = 0.27; NMP/Py = 5; [TPP]/[pABA] = 0.6; $T = 115°C$.

Effect of salt in the synthesis of PPTA[2]

$LiCl_2$ (% w/v)	$CaCl_2$ (% w/v)	LiCl + $CaCl_2$ (% w/v)	η_{inh} (dl g^{-1})
2.7	0.0	2.7	0.32*
0.7	2.0	2.7	0.21*
0.0	3.5	3.5	0.24*
5.5	0.0	5.5	1.22†
6.7	0.0	6.7	1.16†
0.0	6.7	6.7	1.26†
1.7	5.0	6.7	6.84†

*[TA] = 0.125; NMP/Py = 1.5; [TPP]/[TA] = 2.0.
†[TA] = 0.083; NMP/Py = 5; [TPP]/[TA] = 2.0.

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Effect of reactant ratios in the synthesis of PBA[2]

[TPP]/[pABA]	η_{inh} (dl g^{-1})
0.4	0.31*
0.6	2.00*
0.8	1.80*
1.0	1.26*
0.4	0.10†
0.6	1.53†
0.8	1.38†
1.0	1.40†

*Yamakazi conditions: [pABA] = 0.75; NMP/Py = 3; 3.7% LiCl.
†Higashi conditions: [pABA] = 0.27; NMP/Py = 5; 1.7% LiCl; 5.0% $CaCl_2$; $T = 115°C$.

Effect of reactant ratios in the synthesis of PPTA[2]

[TPP]/[TA]	η_{inh} (dl g^{-1})
1.3	0.24*
1.7	0.36*
2.0	0.31*
2.3	0.38*
2.0	6.84†
2.2	8.15†
2.4	6.89†

*Yamakazi conditions: [TA] = 0.125; NMP/Py = 1.5; 2.7% LiCl; T = 115°C.
†Higashi conditions: [TA] = 0.083; NMP/Py = 5; 1.7% LiCl; 5.0% $CaCl_2$.

Effect of temperature in the synthesis of PBA[2]

Temperature (°C)	η_{inh} (dl g^{-1})*
105	1.70
110	1.66
115	2.19
120	1.53

*Yamakazi conditions: [pABA] = 0.27; NMP/Py = 5; [TPP]/[pABA] = 0.6; 6.7% LiCl.

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Effect of temperature in the synthesis of PPTA[2]

Temperature (°C)	η_{inh} (dl g^{-1})
100	0.28*
110	0.36*
115	0.31*
120	0.37*
107	7.71†
115	8.15†
122	6.27†

*Yamakazi conditions: [TA] = 0.125; NMP/Py = 1.5, [TPP]/[TA] = 2.0, 2.7% LiCl.)
†Higashi conditions: [TA] = 0.083; NMP/Py = 5, [TPP]/[TA] = 2.2; 1.7% LiCl, 5.0% $CaCl_2$.)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight of repeat unit	g mol^{-1}	Poly(*p*-phenylene terephthalamide)	240.2	—
Typical polydispersity index ($M_z : M_w : M_n$)	g mol^{-1} ratios	—	$>4.5\,M_z : 1.6\,M_w : 1\,M_n$	(3)
			$>5.3\,M_z : 1.57\,M_w : 1\,M_n$	(3)
			$M_w : M_n = 1.85$ ($M_w = 12{,}300$)	(4)
			$M_w : M_n = 1.63$ ($M_w = 6{,}300$)	(4)
			$M_w : M_n = 1.37$ ($M_w = 5{,}300$)	(4)
Morphology in multiphase systems	—	Composites	Rods (in weaves, fibers, etc.)	—
Raman (characteristic absorption frequencies)	cm^{-1}	Kevlar 29, 49 fibers		(5)
		NC torsion, CC out of plane bending	92 (m)	
		CC in plane bending; ring torsion	106 (m)	
		NH out of plane bending; NC torsion	225 (w)	
		CC in plane bending; CO out of plane bending	265 (w)	
		CC out of plane bending; ring asymmetric torsion	414 (w)	
		CC ring in plane deformation	629 (w)	
		CH out of plane deformation, CO bending	695 (w)	
		Amide V	710 (w)	
		CO in plane bending; ring asymmetric CH deformation; CN stretching	733 (w)	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Raman (characteristic absorption frequencies)	cm^{-1}	CH out of plane deformation; CCC ring puckering deformation	788 (m)	(5)
		1:4 substituted ring deformation	815 (vw)	
		CH out of plane deformation; ring CC stretching, ring bending, and ring torsion	843 (w)	
		Ring out of plane bending	915 (m)	
		ω_4 ring and ring CH deformation	1,182 (m)	
		ω_4 ring and ring CH in plane deformation	1,190 (sh)	
		NH bending, CH stretching	1,277 (s)	
		Ring CH bending	1,328 (s)	
		ω_3 symmetric ring puckering/aromatic CH in plane bending	1,412 (vw)	
		ω_{14} ring vibration; ring CH bending	1,517 (m)	
		Amide II vibration, δ(NH) and ν(CN)	1,569 (w)	
		ω_2 (aromatic ring) CC stretching vibration	1,611 (vs)	
		Amide 1 (C=O) stretching	1,647 (m)	

Raman depolarization ratios[5]

$\Delta\nu$ (cm^{-1})	Kevlar $\rho_\perp$	Kevlar 29 $\rho_\perp$	Kevlar 49 $\rho_\perp$
1,182	0.54 ± 0.02	0.56 ± 0.02	0.30 ± 0.01
1,190	0.55 ± 0.02	0.56 ± 0.02	0.32 ± 0.01
1,277	0.57 ± 0.01	0.56 ± 0.01	0.32 ± 0.01
1,328	0.56 ± 0.01	0.54 ± 0.01	0.30 ± 0.01
1,412	0.55 ± 0.05	0.57 ± 0.05	–
1,517	0.57 ± 0.02	0.54 ± 0.02	0.32 ± 0.01
1,569	0.64 ± 0.05	0.62 ± 0.05	0.33 ± 0.04
1,611	0.53 ± 0.01	0.55 ± 0.01	0.30 ± 0.01
1,647	0.53 ± 0.02	0.56 ± 0.02	0.30 ± 0.01

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
X-ray photoelectron (XPS)	eV	Kevlar 29, 49 fibers	C 1s = 284.6 (intense) O 1s = 530.3 (intense)	(6)
		Valence band XPS is more sensitive to surface functionalized species, although the surface appears to be identical to the bulk	N 1s = 399.7 (intense) C(KVV) = 990 (weak Auger) N(KVV) = 873 (weak Auger) O(KVV) = 745 (weak Auger)	

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PROPERTY	UNITS	CONDITIONS		VALUE		REFERENCE
Bragg spacings	—	*hkl*	*d*-value (nm)	2θ (degree) ($\lambda = 0.1542$ nm)	Intensity	(7)
		110	0.4327	20.53	vs	
		200	0.3935	22.60	vs	
		020	0.2590	34.63	vw	
		310	0.2340	38.46	m	
		220	0.2163	41.75	w	
		011	0.4807	18.46	vw	
		111	0.4102	21.66	ms	
		211	0.3045	29.33	s	
		021	0.2539	35.35	w	
		121	0.2417	37.20	vw	
		311	0.2302	39.12	vw	
Thermal expansion coefficients	K^{-1}	Kevlar 29 fiber ASTM D3379-75e axial thermal expansion coefficient		-3.2×10^{-6} $-2 \times 10^{-6} < \alpha < -4 \times 10^{-6}$		(8)
Solvents	Concentrated H_2SO_4 Polar aprotic solvents (NMP/DMAc) w ~5 wt% $LiCl_2$					—
Nonsolvents	Aromatics, aliphatics, water, alcohols, ethers, esters					—

Chemical resistances[9]

Chemical*	Conc. (%)	Temp. (°C)	Time (h)	Effect†
Acids				
Acetic	99.7	21	24	None
Acetic	40	21	1,000	Slight
Acetic	40	99	100	Appreciable
Benzoic	3	99	100	Appreciable
Chromic	10	21	1,000	Appreciable
Formic	90	21	100	None
Formic	40	21	1,000	Moderate
Formic	90	99	100	Degraded
Hydrobromic	10	21	1,000	Appreciable
Hydrochloric	37	21	24	None
Hydrochloric	10	21	100	Appreciable
Hydrochloric	10	71	10	Degraded
Hydrofluoric	10	21	100	None
Nitric	1	21	100	Slight
Nitric	10	21	100	Appreciable
Nitric	70	21	24	Appreciable
Oxalic	10	99	100	Appreciable
Phosphoric	10	21	100	None
Phosphoric	10	21	1,000	Slight

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Chemical*	Conc. (%)	Temp. (°C)	Time (h)	Effect†
Acids				
Phosphoric	10	99	100	Appreciable
Salicylic	3	99	1,000	None
Sulfuric	10	21	1,000	Moderate
Sulfuric	10	21	100	None
Sulfuric	10	100	10	Appreciable
Sulfuric	70	21	100	Moderate
Bases				
Ammonium hydroxide	28.5	21	24	None
Ammonium hydroxide	28	21	1,000	None
Potassium hydroxide	50	21	24	None
Sodium hydroxide	40	21	100	None
Sodium hydroxide	10	21	1,000	None
Sodium hydroxide	10	99	100	Degraded
Sodium hydroxide	10	100	10	Appreciable
Sodium hypochlorite	0.1	21	1,000	Degraded
Salt solutions				
Copper sulfate	3	21	1,000	None
Copper sulfate	3	99	100	Moderate
Ferric chloride	3	99	100	Appreciable
Sodium chloride	3	21	1,000	None
Sodium chloride	10	99	100	None
Sodium chloride	10	121	100	Appreciable
Sodium phosphate	5	99	100	Moderate
Organic solvents				
Carbon tetrachloride	100	Boiling	100	Moderate
Ethylene glycol/H_2O	50/50	99	1,000	Moderate
Brake fluid	100	113	100	Moderate

*Chemicals not listed in the table have no noticeable effect.
†Effect on breaking strength: none = 0–10% stress loss; slight = 11–20% stress loss; moderate = 21–40% stress loss; appreciable = 41–80% stress loss; degraded = 81–100% stress loss.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Phase diagrams	Solid/anisotropic solution/isotropic solution regimes			(10, 11)
Fractionation	—	Chromatography		
		90% H_2SO_4	Preparative GPC, silica gel	(12)
		96% H_2SO_4	GPC	(13)
		Tetrahydrofuran	GPC, shodex	(13)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Mark-Houwink parameters: K and a	$K = \text{ml g}^{-1}$ a = None	(a values greater than 1.7 indicate strong aggregation effects)		(14)
		$1.0 < a < 1.85$		
		PBA $3{,}100 < M_w < 13{,}000$	$K = 2.14$	
		Concentrated H_2SO_4, 25°C	$a = 1.203$	
Persistence length	Å	96% sulfuric acid, 25°		
		Electric birefringence, Kerr effect	PPTA = 300	(15)
		Light scattering, R_g	PBA = 400	(12)
			PPTA = 200	(12)
		Light scattering, depolarization ratio	PPTA = 150	(16)
		Light scattering depolarization	PPTA = 287	(17)
		Light scattering	PPTA = 450	(18)
		Light scattering	PBA = 600	(13)
			PPTA = 200	(13)
		Viscosity	PBA = 400	(13)
			PPTA = 150	(13)
		Flow birefringence	PBA = 1050	(19)
			PPTA = 650	(19)
		Flow birefringence	PBA = 435	(20)
			PPTA = 275	(20)
		Flow birefringence	PBA = 325	(21)
		Flow birefringence	PPTA = 185	(22)
		Depolarization ratio, unfractionated	PPTA = 1020	(14)
		Depolarization ratio, unfractionated oligomer $M_w < 10{,}900$	PPTA = 306	(14)
Viscosity vs. shear rate	poise	Kevlar-100% H_2SO_4 solutions, 25°C		(1)
		0.5 wt% Kevlar, $10^{-1}\,s^{-1} < \gamma < 10\,s^{-1}$	$\eta = 2.1$	
		6–8 wt% Kevlar, $10^{-2}\,s^{-1} < \gamma < 10^{1}\,s^{-1}$	$\eta = 1{,}100$	
		10 wt% Kevlar		
		$\gamma = 10^{-2}\,s^{-1}$	$\eta = 30{,}000$	
		$\gamma = 10^{-1}\,s^{-1}$	$\eta = 6{,}000$	
		$\gamma = 10^{0}\,s^{-1}$	$\eta = 800$	
		$\gamma = 10^{1}\,s^{-1}$	$\eta = 300$	
Viscosity vs. shear stress	poise	Kevlar-100% H_2SO_4 solutions, 25°C		(1)
		6–8 wt% Kevlar		
		10^{1} dynes $cm^{-2} < \sigma_{12} < 10^{4}$ dynes cm^{-2}	$\eta = 1{,}100$	
		10 wt% Kevlar		
		$\sigma_{12} = 5 \times 10^{2}$ dynes cm^{-2}	$\eta = 40{,}000$	
		$\sigma_{12} = 10^{3}$ dynes cm^{-2}	$\eta = 4{,}000$	
		$\sigma_{12} = 3 \times 10^{3}$ dynes cm^{-2}	$\eta = 200$	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Normal stress vs. shear rate	dynes cm^{-2}	Kevlar-100% H_2SO_4 solutions, 25°C		(1)
		6 wt% Kevlar		
		$\gamma = 2\,s^{-1}$	$N_1 = 3{,}000$	
		$\gamma = 8\,s^{-1}$	$N_1 = 10^5$	
		8 wt% Kevlar		
		$\gamma = 1\,s^{-1}$	$N_1 = 5{,}000$	
		$\gamma = 8\,s^{-1}$	$N_1 = 10^5$	
		10 wt% Kevlar		
		$\gamma = 0.7\,s^{-1}$	$N_1 = 2 \times 10^5$	
		$\gamma = 1\,s^{-1}$	$N_1 = 5 \times 10^4$	
		$\gamma = 8\,s^{-1}$	$N_1 = 8 \times 10^4$	
Bond lengths	Å	C(1)–C(2)	1.47	(23)
		C(2)–C(3)	1.39	
		C(3)–C(4)	1.39	
		C(1)–O(1)	1.24	
		C(1)–N(1)	1.34	
		N(1)–H(1)	1.00	
		N(1)–C(8)	1.42	
		C(8)–C(9)	1.39	
		C(9)–C(10)	1.39	
		C–H(phenyl)	1.00	
Bond angles	Degrees	C(4)–C(3)–C(2)	120	(24)
		C(3)–C(2)–C(7)	120	
		C(3)–C(2)–C(7)	120	
		C(7)–C(2)–C(1)	120	
		C(2)–C(1)–N(1)	120	
		C(2)–C(1)–O(1)	120	
		N(1)–C(1)–O(1)	115	
		C(1)–N(1)–H(1)	123	
		C(8)–N(1)–H(1)	120	
		N(1)–C(8)–C(9)	117	
		N(1)–C(8)–C(13)	120	
		C(9)–C(18)–C(13)	120	
		C(8)–C(9)–C(10)	120	
Torsional potential diagram	–	–	–	(23)
Persistence length	Å	Extended all *trans* conformation (upper bound)		(23)
		PBA (no temp. dependence)	900	
		PPTA (no temp. dependence)	410	
		Rotatable amide group (lower bound)		
		PBA at 200 K	200	
		PBA at 600 K	~0	
		PBA at 300 K	100	
		PPTA at 200 K	200	
		PPTA at 600 K	~0	
		PPTA at 300 K	100	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Maximum temperature for liquid crystallinity	K	–	600	(23)
Lattice	–	–	Monoclinic (pseudo orthorhombic)	(24)
Space group	–	–	$P2_{1/n}$–C_{2h}	(24)
Chain conformation	–	Extended *trans*	Modification 1,2	(24)
Unit cell dimensions	Å	–	$a = 7.80$, $b = 5.19$, c (fiber axis) $= 12.9$	(24)
Unit cell angles	Degrees	–	$\gamma = 90$	(24)
Unit cell contents (number of repeat units)	–	–	2 chains/cell	(24)
Degree of crystallinity	%	Kevlar 49 H_2SO_4 cast film		(25)
		Annealed 100°C, 2 h	0.22	
		Annealed 200°C, 2 h	0.38	
		Annealed 300°C, 2 h	0.45	
Polymorphs	–	Modification I (PBA-$LiCl_3$-DMAc) Modification II (PBA-$LiCl_2$ cocrystal) Modification III (PBA) Lyotropic nematic		(26)
Glass transition temperature	K	–	698	(27)
Melting point	K	In general beyond decomposition temperature (500°C)		(26)
		Modification III(PBA)	827	
Super-T_g transition temperatures	K	Modification I (PBA-$LiCl_3$-DMAc) Modification II (PBA-$LiCl_2$ cocrystal) Modification III (PBA)	I–II = 487 K I-amorphous = wash with H_2O II–III = anneal at 748 K, then cool II–III = wash with H_2O I–III = wash with H_2O and anneal >673 K	(26)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Super-T_g transition temperatures	K	Modification III (PBA)	II-nematic = 748 K III-nematic = 827 III-amorphous = heat to 873 K and cool	(26)
Sub-T_g transition temperatures	–	$f = 10{,}000\,Hz$ $T_\gamma = 291\,K$ $f = 10{,}000\,Hz$ $T_{\gamma^*} = 417\,K$ $f = 110\,Hz$ $T_\beta = 733\,K$ $f = 110\,Hz$ $T_\gamma = 333\,K$ $f = 110\,Hz$ $T_\delta = 243\,K$ $f \sim 1\,Hz$ $T_\beta = 816\,K$ $f \sim 1\,Hz$ $T_\gamma = 235\,K$ $f \sim 1\,Hz$ $T_{\gamma^*} = 440\,K$ $f \sim 1\,Hz$ $T_\delta = 115\,K$	$E_{a,\gamma} = 63\,kJ\,mol^{-1}$ $E_{a,*^*} = 92\,kJ\,mol^{-1}$ $E_{a,\beta} = 767\,kJ\,mol^{-1}$ $E_{a,\gamma} = 204\,kJ\,mol^{-1}$ $E_{a,\delta} = 52\,kJ\,mol^{-1}$ $E_{a,\beta} = 813\,kJ\,mol^{-1}$ $E_{a,\gamma} = 54\,kJ\,mol^{-1}$ $E_{a,\gamma^*} = 83\,kJ\,mol^{-1}$ $E_{a,\delta} = 21\,kJ\,mol^{-1}$	(28) (28) (29) (29) (30) (30) (30) (30) (30)
Polymers with which they are compatible	–	None known. Surface modifications for composites.		–
Tensile modulus	MPa	Ultimate Modulus D Kevlar 29 fiber Kevlar 49 fiber Kevlar 149 fiber Twaron LM fiber Twaron HM fiber	$\sim 165 \times 10^3$ 83×10^3 124×10^3 161×10^3 76×10^3 105×10^3	(9)
Crystal modulus	MPa	Kevlar, Twaron fibers XRD Kevlar, Twaron fibers	156×10^3 220×10^3	–
Shear modulus	MPa	Kevlar fibers in tension and compression	1,150	–
Storage modulus	MPa	Kevlar/100% H_2SO_2 solutions 8 wt% Kevlar $\omega = 0.02\,Hz$ $\omega = 0.1\,Hz$ $\omega = 0.5\,Hz$ $\omega = 1\,Hz$ $\omega = 5\,Hz$ $\omega = 10\,Hz$ 10 wt% Kevlar $\omega = 0.01\,Hz$ $\omega = 0.1\,Hz$ $\omega = 0.5\,Hz$ $\omega = 1\,Hz$ $\omega = 5\,Hz$ $\omega = 10\,Hz$	 $G' = 1 \times 10^{-9}$ $G' = 2 \times 10^{-9}$ $G' = 1 \times 10^{-8}$ $G' = 2 \times 10^{-8}$ $G' = 7 \times 10^{-8}$ $G' = 2 \times 10^{-7}$ $G' = 4 \times 10^{-7}$ $G' = 5 \times 10^{-7}$ $G' = 6 \times 10^{-7}$ $G' = 7 \times 10^{-7}$ $G' = 1 \times 10^{-6}$ $G' = 2 \times 10^{-6}$	 (1)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Loss tangent vs. frequency	–	Kevlar/100% H_2SO_4 solutions		(1)
		8 wt% Kevlar		
		$\omega = 0.02$ Hz	$\tan\delta = 2$	
		$\omega = 0.05$ Hz	$\tan\delta = 3$	
		$\omega = 0.1$ Hz	$\tan\delta = 4$	
		$\omega = 0.5$ Hz	$\tan\delta = 5$	
		$\omega = 1$ Hz	$\tan\delta = 6$	
		$\omega = 5$ Hz	$\tan\delta = 5$	
		$\omega = 10$ Hz	$\tan\delta = 3$	
		10 wt% Kevlar		
		$\omega = 0.01$ Hz	$\tan\delta = 0.3$	
		$\omega = 0.1$ Hz	$\tan\delta = 0.4$	
		$\omega = 1$ Hz	$\tan\delta = 0.6$	
		$\omega = 10$ Hz	$\tan\delta = 0.9$	
Tensile strength	MPa	LC solution spun Kevlar fibers	2,000–3,000	–
Maximum extensibility $(L/L_0)_r$	%	Kevlar 29 fiber in tension	4.0	(27)
		Kevlar 49 fiber in tension	2.5	(9)
Fracture stress	MPa	Fiber in tension		–
		Kevlar 29 fiber	2,500	
		Kevlar 49 fiber	2,300	
		Kevlar 149 fiber	1,700	
		Twaron LM fiber	3,400	
		Twaron HM fiber	2,800	
Fracture strain	%	Fiber in tension		–
		Kevlar 29 fiber	2.5	
		Kevlar 49 fiber	1.8	
		Kevlar 149 fiber	1.0	
		Twaron LM fiber	2.4	
		Twaron HM fiber	2.5	
Compressive strength	Four point bend of a fiber embedded in a PMMA matrix			–
Tenacity (fiber)	MPa	Kevlar 49	2,800	(27)
		Kevlar 29	2,800	
Poisson ratio	–	–	0.36	9)
Force-temperature relationships	–	Kevlar 49 fibers in ASTM D3379-75e; force-temperature cycling 5 gpd applied load-heat to 300°C, cool to ambient	Critical temp. for stress-drop decreases from ~493 K to 198 K as 1.0 gpd stress applied	(8)
Thermal expansivity		Axial expansivity, Kevlar fiber		(6)
		At 200 K	−0.8	
		At 450 K	−0.7	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Index of refraction n	—	$n_{\perp}$ = index of refraction perpendicular to fiber axis Kevlar 29	2.0499 (center of fiber) 2.0853 (fiber edge)	(31)
		$n_{\|\|}$ = index of refraction parallel to fiber axis	1.5886 (center of fiber) 1.6504 (edge of fiber)	
Refractive index increment dn/dc	$ml\,g^{-1}$	All values at 25°C using a 633 nm source		
		Chlorosulfonic acid	0.275	(32)
		Chlorosulfonic acid + 0.01 M $LiClSO_3$	0.287	(33)
		H_2SO_4	0.278	(32)
		96% H_2SO_4	0.309 (546 nm source)	(13)
		Methane sulfonic acid	0.254	(33)
Segmental polarizability $(\alpha_1 - \alpha_2)$, $(\alpha_{\|\|} - \alpha_{\perp})$	cm^3	Sulfuric acid (includes form effect)	$(\alpha_1 - \alpha_2) = +5,250 \times 10^{-25}$ $(\alpha_{\|\|} - \alpha_{\perp}) = +206 \times 10^{-25}$	(34, 35)
		Copolymer with poly(benzamide) 1/9 PPTA/PBA ratio	$(\alpha_1 - \alpha_2) = +4,380 \times 10^{-25}$	
Segmental optical anisotropy δ_0^2	—	Light depolarization, unfractionated polymer	PPTA = 0.266	(14)
		Light depolarization, unfractionated oligomers, $M_w < 10,900$	PPTA = 0.357	
Optical anisotropy Δ^2	—	Depolarization ratio, fractionated PPTA		(16)
		$M = 1,560\ g\,mol^{-1}$	0.290	
		$M = 2,160\ g\,mol^{-1}$	0.223	
		$M = 2,760\ g\,mol^{-1}$	0.184	
		$M = 3,480\ g\,mol^{-1}$	0.154	
		$M = 4,560\ g\,mol^{-1}$	0.30	
		$M = 6,600\ g\,mol^{-1}$	0.103	
		$M = 7,920\ g\,mol^{-1}$	0.094	
		Unfractionated PPTA		
		$M_w = 2,160\ g\,mol^{-1}$	0.270	(16)
		$M_w = 4,320\ g\,mol^{-1}$	0.177	(16)
		$M_w = 1,680\ g\,mol^{-1}$	0.294	(13)
		$M_w = 4,500\ g\,mol^{-1}$	0.183	(13)
		$M_w = 9,350\ g\,mol^{-1}$	0.164	(13)
		$M_w = 19,700\ g\,mol^{-1}$	0.111	(13)
		$M_w = 35,000\ g\,mol^{-1}$	0.105	(13)
		$M_w = 43,500\ g\,mol^{-1}$	0.094	(13)
		$M_w = 63,000\ g\,mol^{-1}$	0.084	(13)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Surface free energy	$mJ\,m^{-1}$	γ_s^d dispersive	40 ± 4	–
Heat of adsorption	$kJ\,mol^{-1}$	IGC adsorption		–
		Epoxystyrene on Kevlar 29	45 ± 3	
		Aniline on Kevlar 29	11	
Specific free energy of interaction	$kJ\,mol^{-1}$	ΔG_{sp}		–
		Epoxystyrene on Kevlar 29	5.6	
		Aniline on Kevlar 29	11	
Heat of hydration	$kJ\,mol^{-1}$	ΔH_H of Kevlar 29 Fiber	−60	–

Permeability coefficient (Kevlar 49 film, H_2SO_4 cast)* [(25)]

Gas (at 35°C)	Annealed 2 h at			Amorphous Kevlar/Nomex copolymer
	200°C	100°C	300°C	
H_2	10,000	10,000	6,000	–
He	11,500	11,000	10,100	–
CO_2	1,020	1,020	500	–
O_2	220	220	80	2,579
N_2	20	35		–

*Values given in cm^2(STP) $cm\,s^{-1}\,cm^{-2}\,cmHg^{-1}$ ($\times 10^{-15}$)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Temperature dependence of permeability coefficient *P*	cm^2(STP) $cm\,s^{-1}\,cm^{-1}$ cmHg	Linear (Arrhenius) decay for H_2 and CO_2		(25)
		Amorphous Kevlar/Nomex copolymer		
		25°C	5.8×10^{-12}	
		65°C	0.9×10^{-11}	
		Kevlar 49 H_2SO_4 cast film		
		Annealed 100°C, 2 h		
		25°C	8×10^{-13}	
		65°C	1.5×10^{-12}	
		Annealed 200°C, 2 h		
		25°C	1×10^{-12}	
		65°C	3×10^{-12}	
		Annealed 300°C, 2 h		
		25°C	3×10^{-13}	
		65°C	1×10^{-12}	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Arrhenius activation energy for permeability coefficient E_P	kcal mol^{-1}	Carbon dioxide		(25)
		Amorphous Kevlar/Nomex copolymer	5.5	
		Kevlar 49 H_2SO_4 cast film		
		Annealed 100°C, 2 h	5.6	
		Annealed 200°C, 2 h	6.3	
		Annealed 300°C, 2 h	5.9	
Diffusion coefficient	$cm^2\,s^{-1}$	Water into Kevlar 29 fiber	0.95×10^{-12}	(36)
		Kevlar 29 H_2SO_4 film	(See table below)*	(25)

Gas	Kevlar 49 film, annealed 2 h at			Amorphous Kevlar/Nomex copolymer
	100°C	200°C	300°C	
H_2	~200	~200	~200	–
He	~800	~800	~800	–
CO_2	0.4	0.42	0.2	–
O_2	0.81	1.10	0.62	9.26
N_2	0.18	0.22	–	–

*Values given in $cm^2\,s^{-1}$ ($\times 10^{10}$)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Temperature dependence of diffusion coefficient D	$cm^2\,s^{-1}$	Linear (Arrhenius) Relationship for H_2 and CO_2		(25)
		Amorphous Kevlar/Nomex copolymer		
		25°C	2×10^{-10}	
		65°C	1.62×10^{-9}	
		Kevlar 49 H_2SO_4 cast film		
		Annealed 100°C, 2 h		
		25°C	2×10^{-11}	
		65°C	1×10^{-10}	
		Annealed 200°C, 2 h		
		25°C	2.2×10^{-11}	
		65°C	1.3×10^{-10}	
		Annealed 300°C, 2 h		
		25°C	8×10^{-12}	
		65°C	5×10^{-11}	
Arrhenius activation energy for diffusion coeffient E_D	kcal mol^{-1}	Carbon dioxide		–
		Amorphous Kevlar/Nomex copolymer	10.5	
		Kevlar 49 H_2SO_4 cast film		
		Annealed 100°C, 2 h	9.2	
		Annealed 200°C, 2 h	9.4	
		Annealed 300°C, 3 h	10.1	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of sorption ΔH_s	kcal mol^{-1}	Carbon dioxide		(25)
		Amorphous Kevlar/Nomex copolymer	−5.0	
		Kevlar 49 H_2SO_4 cast film		
		Annealed 100°C, 2 h	−3.6	
		Annealed 200°C, 2 h	−3.1	
		Annealed 300°C, 2 h	−4.2	
Thermal conductivity	W m^{-1} K^{-1}	Phonon propagation in Kevlar 49	10	(37)
	W m^{-1} K^{-2}	5–250 K	$dK/dT = 1$	(37)
	W m^{-1} K^{-1}	Axial thermal conductivity, 125–250 K	20–30	(38)
Biodegradability, effective microorganisms	–	Degradation by *A. flavus*	Kevlar 29 degrades more than Kevlar 49	(39)
Degradation mechanisms		UV radiation	Critical UV window = 300–500 nm	(9)
		UV reduction of M_n	Photolytic-degradation kinetics	(40, 41)
		Hydrolytic	Concentrated H_2SO_4	(42)
			Humidity, temperature	(43)
		Atomic oxygen/UV	UV resistance mechanism	(44)
		Laser	488 nm Ar ion laser beam	(45)
		Photolytic	Simulated sunlight	(46)
		Thermal	Radical homolytic	(47, 48)
			High pressure	(49)
			ESR radical study	(50)
		Photochemical	Smog, ozone, temp., RH	(51)
			Oxidation in H_2SO_4	(52, 53)
Maximum use temperature	K	In air	573–623	(9)
Decomposition temperature	K	In air	700–755	(9)
Decomposition products	K	H_2, CO, CO_2, HCN, H_2O, benzene, toulene, benzonitrile	573–773	(9, 54)
		CO_2, H_2O, CO	643–723	(9, 55)
		Benzene, HCN, benzonitrile, H_2	723–823	(9, 55)
Heat of combustion	J kg^{-1}	–	35×10^6	(9)
Limiting oxygen index	–	–	29	(9)

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Kraton D1100 SBS

C. M. ROLAND

CHEMICAL NAME Linear styrene-butadiene-styrene triblock copolymer

STRUCTURE
$$[-\underset{\displaystyle C_6H_5}{\underset{|}{C}H}-CH_2-]_m-[-CH_2-CH{=}CH-CH_2-]_n-[-\underset{\displaystyle C_6H_5}{\underset{|}{C}H}-CH_2-]_m$$

CLASS Chemical copolymers; unsaturated thermoplastic elastomers

MAJOR APPLICATIONS Asphalt modifiers, adhesives, sealants, coatings, footwear, polymer modifers.

PROPERTIES OF SPECIAL INTEREST In general, thermoplastic elastomers (TPE) provide the mechanical properties of rubber in combination with the processing characteristics of plastics; recyclable; Kraton D's are the lowest cost TPE ($\geq$\$0.85 lb^{-1}).

OTHER COMPARABLE COMMERCIAL MATERIALS Cariflex (Shell), K-Resin and Solprene (Phillips), Dexco (Dow/Exxon), Europrene (Enichem), Tufprene and Asaprene (Asahi), Stereon (Firestone), Dynaflex (GLS), Vitacom (British Vita), European (Enoxy), Finaprene (Petrofina), Calprene (Calatrava).

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Price	$\$\ lb^{-1}$	–	0.85–1.30		(1)
Specific gravity	–	–	0.94		(2)
Glass transition temperature T_g	K	–	178		(3)
Styrene/rubber	wt. $wt.^{-1}$	–	31/69		(4)
300% modulus	MPa	ASTM D412	2.8		(2, 4)
Elongation	%	ASTM D412	880		(2, 4)
Tensile strength	MPa	ASTM D412	32		(2, 4)
Stress relaxation	Relaxed/initial	RT (9% strain)	0.58		(5)
Processing temperature	K	–	423–473		(6)
			Kraton D1101	Kraton D1102	
S/B/S	wt%	–	15/70/15	14/72/14	(2, 7)
Physical form	–	–	Porous pellet, powder	Porous pellet	(7)
Brookfield viscosity	–	Toluene at 77°F	4,000	1,200	(7)
Hardness	Shore A	–	71	62	(2)
Melt index	–	(ASTM D1238)	<1	6[(1)] 11[(2)]	(2, 7)

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Chemical resistance	–	Acids	Good		(8)
		Bases	Good		
		Aromatics	None		
		Aliphatics	None		
		Oil in water	Good		
		Water in oil	None		
Gas permeability of D1101					(9)
Permeability coefficient	SI	O_2	2×10^{-12}		
		CO_2	8×10^{-12}		
Transmission rate	$cm^2\ s^{-1}$	O_2	2×10^{-7}		
		CO_2	8×10^{-7}		
Water permeability of D1101					(9)
Permeability coefficient	SI	–	2.7×10^{-10}		
Transmission rate	$g\ cm^{-2}\ s^{-1}$	–	3.0×10^{-8}		
Wet chemical identification of Kraton D	–	Step	Observed color		(10)
		Pyrolysis vapors passed into Burchfield reagent	Yellow green		
		Added methanol and boiled	Green		
Effect of solvent on D1101 viscosity					(11)
Solubility parameter	$(cal\ cc^{-1})^{1/2}$	Solvent			
		MIBK	8.35		
		Toluene	8.59		
		Tetralin	8.76		
		o-Xylene	9.03		
		Cyclohexanone	9.62		
Intrinsic viscosity	$dl\ g^{-1}$	Solvent			
		MIBK	0.31		
		Toluene	1.04		
		Tetralin	1.17		
		o-Xylene	0.91		
		Cyclohexanone	0.44		
			Kraton D/Asphalt blends		(12)
Kraton D1101	wt%	–	67	50	
Asphalt	wt%	–	33	50	
Mechanical properties					
300% Modulus	MPa	–	1.8	0.8	
Elongation	%	–	1,700	1,500	
Tensile strength	MPa	–	17.5	9.7	
Hardness	Shore A	–	46	36	
Permanent set	%	–	50	30	

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PROPERTY	UNITS	CONDITIONS	VALUE			REFERENCE
Softening point	K	Kraton D1101 (wt%) in asphalt/oil blends				(12)
		0	311			
		2	335			
		4	347			
		6	354			
		8	360			
		10	365			
		12	371			
Adhesion of 10% Kraton D1101 in asphalt/oil blend	180 peel strength (lb in^{-1})	Adherend				(12)
		Itself	5.5			
		Smooth plywood	6.8			
		Ground steel	5.6			
		Concrete	7.0			
		Galvanized iron	5.4			
Kraton D blends with HIPS	As indicated	HIPS (wt%)	100	90	90	(13)
		Kraton D1101 (wt%)	–	10	–	
		Kraton 1102 (wt%)	–	–	10	
		1/8 in notched Izod (N)	85	150	120	
		Flex modulus (GPa)	2,100	1,800	1,900	
Supplier	Shell Chemical Co., One Shell Plaza, P.O. Box 2463, Houston, Texas 77252-2463, USA					

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Kraton G1600 SEBS

C. M. ROLAND

CHEMICAL NAME Linear styrene-(ethylene-butylene)-styrene triblock copolymer

STRUCTURE $[-\underset{C_6H_5}{\underset{|}{C}H}-CH_2-]_m-[[-CH_2-CH_2]_x-[\underset{CH_2-CH_3}{\underset{|}{C}H}-CH_2]_y]_n-[-\underset{C_6H_5}{\underset{|}{C}H}-CH_2-]_m$

CLASS Chemical copolymers; saturated thermoplastic elastomers

MAJOR APPLICATIONS Asphalt modifiers, adhesives, sealants, coatings, footwear, polymer modifiers, and oil gels.

PROPERTIES OF SPECIAL INTEREST In general, thermoplastic elastomers (TPE) provide the mechanical properties of rubber in combination with the processing characteristics of plastics; recyclable; Kraton G's are low cost TPEs with oxidative and thermal stability, good weathering, and ozone resistance.

OTHER COMPARABLE COMMERCIAL MATERIALS Elexar (Shell), Dexco (Dow/Exxon), Dynaflex (GLS), Vitacom (British Vita), Tekron (Teknor), C-Flex (Concept), Septon (Kuraray), Finaprene (Petrofina), Calprene (Calatrava)

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Price	$ lb^{-1}	Kraton G1650	1.85–2.80		(1)
Specific gravity	—	Kraton G1650	0.91		(2)
Glass transition temperature T_g	K	Kraton G1650, EB block	213		(1)
Molecular weight M_w	g mol^{-1}	Kraton G1650			(3)
		EB block	54,000		
		S block	10,000 (×2)		
			Kraton G1650	Kraton G1652	
S/B/S	wt%	—	15/70/15	15/70/15	(2, 4)
Physical form	—	—	Powder	Powder	(4)
Viscosity	Brookfield	Toluene, 25°C	8,000	1,350	(4)
Hardness	Shore A	—	72	77	(2)
Melt Index	—	ASTM D1238	0	2.5 (463 K) 10 (473 K)	(2, 4)
300% Modulus	MPa	ASTMD412	3.8	5.5	(2)
Elongation	%	ASTMD412	560	520	(2)
Tensile strength	MPa	ASTMD412	26	27	(2)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Chemical resistance	–	Acids	Good	(5)
		Bases	Good	
		Aromatics	Poor	
		Aliphatics	Poor/fair	
		Oil in water	Good	
		Water in oil	Poor/fair	
Gas permeability of Kraton G				(6)
Permeability coefficient	SI	G1650 resin		
		O_2	1.1×10^{-12}	
		CO_2	4.4×10^{-11}	
		G1651 resin		
		O_2	1.0×10^{-11}	
		CO_2	2.9×10^{-11}	
		G1652 resin		
		O_2	1.3×10^{-12}	
		CO_2	4.4×10^{-11}	
Transmission rate	$cm^2\ s^{-1}$	G1650 resin		
		O_2	1.1×10^{-7}	
		CO_2	2.7×10^{-7}	
		G1651 resin		
		O_2	9.8×10^{-8}	
		CO_2	2.8×10^{-7}	
		G1652 resin		
		O_2	1.2×10^{-7}	
		CO_2	3.9×10^{-7}	
Water permeability of Kraton G				(6)
Permeability coefficient	SI	G1650 resin	5.8×10^{-11}	
		G1651 resin	6.6×10^{-11}	
		G1652 resin	8.7×10^{-11}	
Transmission rate	$g\ cm^{-2}\ s^{-1}$	G1650 resin	6.4×10^{-9}	
		G1651 resin	7.3×10^{-9}	
		G1652 resin	9.7×10^{-9}	
Viscosity of Kraton G1650	Pa s	In toluene solutions (wt%)		(7)
		75	6.8×10^{-1}	
		80	1.8×10^{-1}	
		85	3.8×10^{-2}	
		90	5.6×10^{-3}	
		95	7.5×10^{-4}	

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PROPERTY	UNITS	CONDITIONS	VALUE					REFERENCE
Viscosity of Kraton G1650 solutions (15% solids)	Pa s	Solvent						(7)
		Isobutyl isobutyrate	1.4×10^{-1}					
		Ethyl benzene	4.8×10^{-2}					
		Cyclohexane	3.6×10^{-2}					
		Methyl-N-amyl-ketone	1.5×10^{-3}					
		Toluene	4.3×10^{-2}					
Resin and oil compatibility with EB segment	—	Polyterpenes	Incompatible					(8)
		Hydrogenated resin esters	Incompatible					
		Saturated hydrocarbon resins	Compatible					
		Naphthenic oils	Incompatible					
		Paraffinic oils	Compatible					
		Low molecular weight polybutenes	Compatible					
		Aromatic resins	Incompatible					
Kraton G-polypropylene blends	As indicated	Polypropylene (wt%)	100	90	80	90	80	(9)
		Kraton G1650 (wt%)	—	10	20	—	—	
		Kraton G1652 (wt%)	—	—	—	10	20	
		1/8 in. notched Izod (N)	48	64	690	75	520	
		Flex modulus (GPa)	1,500	1,200	940	1,000	890	
Supplier	Shell Chemical Co., One Shell Plaza, P.O. Box 2463, Houston, Texas 77252-2463, USA							

Effect of SEBS level on failure of PET/HDPE 50/50 blends[10]

SEBS (%)	Modulus (MPa)	Yield (MPa)	Elongation (%)
0	1,300	26	3
5	1,200	23	40
10	920	20	130
20	650	18	(no break)

Kraton G modification of mopping asphalts[11]

Property	Units	Type III asphalt	Kraton G modified asphalt
Cold bond (ASTM D5147-91)	K	288	253
Elongation	%	100	1,000
Tensile strength	MPa	0.21	0.69
Puncture sealing	—	Poor	Very good/fast
Ring and ball softening point	K	362	379

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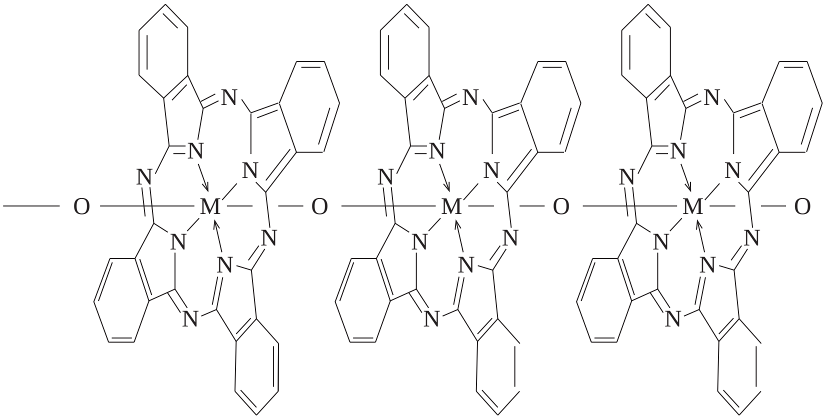
Metallophthalocyanine polymers

MARTEL ZELDIN AND YULI ZHANG

CLASS Cofacial polymers

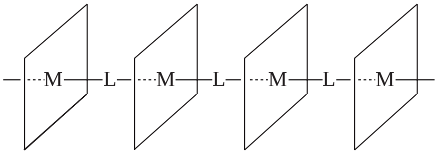
STRUCTURES

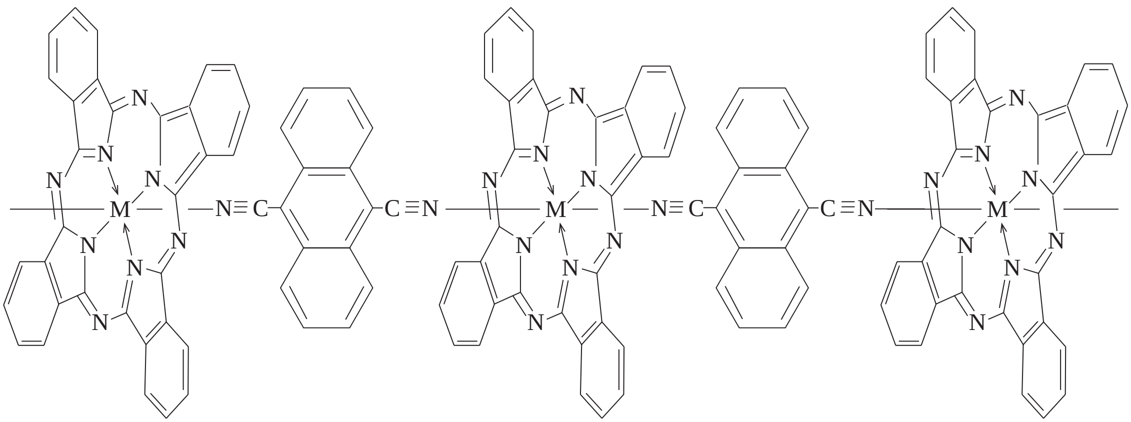
$[M(Pc)O]_n$:



where M = Si, Ge, or Sn; Pc = phthalocyanine.

$[M'(Pc')L]_n$:





where M′ = Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Ru^{2+}, Mn^{2+}, Mn^{3+}, or Cr^{3+}.

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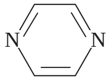
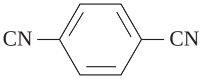
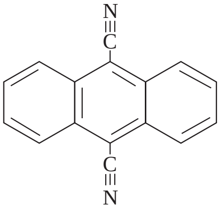
L =



Pyrazine (pyz)



p-Diisocyanobenzene (dib)

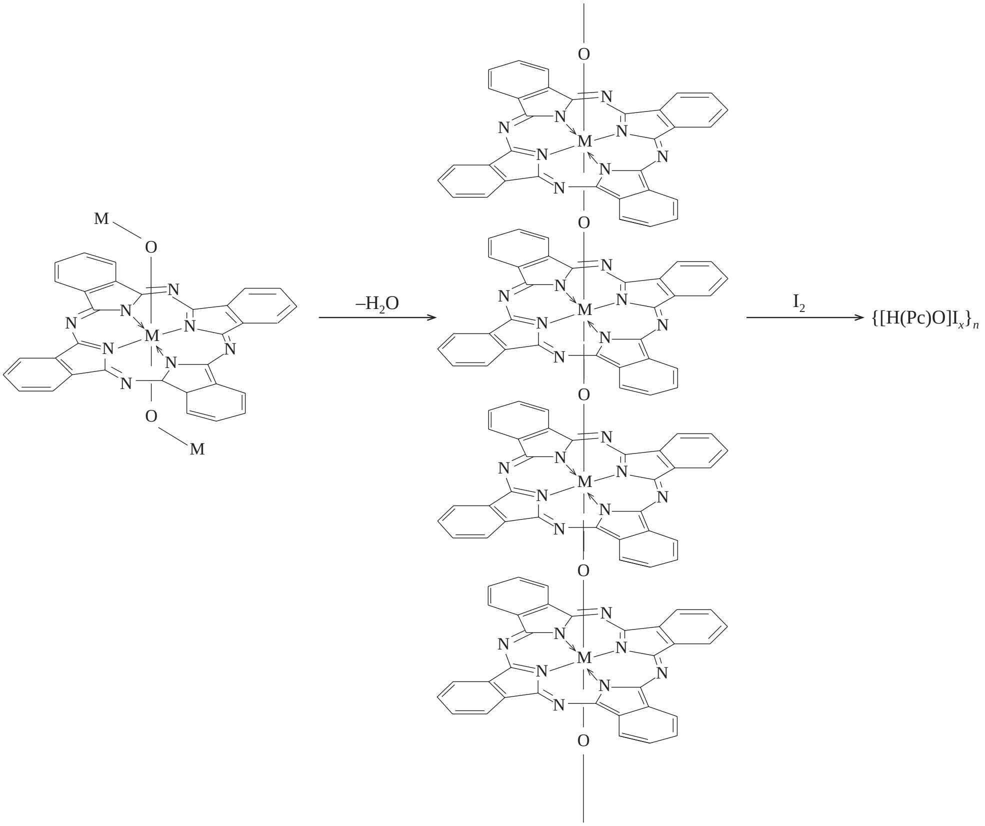


9,10-Diisocyanoanthracene (9,10-dia)

CN^{1-}, or SCN^{1-}.

Pc′ = Pc^{2-}, R_4Pc^{2-}, R_8Pc^{2-}, 1,2-Nc^{2-} (1,2-naphthalocyaninato), 2,3-Nc^{2-} (2,3-naphthalocyaninato), or TBP^{2-}. R = *t*-Bu, Et, OR′ (R′ = $C_5H_{11}-C_{12}H_{25}$) (substituted in the peripheral positions).

SYNTHESIS Condensation of $Si(Pc)(OH)_2$, $Ge(Pc)(OH)_2$, $Sn(Pc)(OH)_2$ to form phthalocyaninato polysiloxanes, polygermyloxanes, and polystannyloxanes.[1–4]



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MAJOR APPLICATIONS Electrical conductors, semiconductors, and materials with photooptical properties.

Electric conductivity

POLYMER	UNITS	*y*	VALUE	REFERENCE
$[Si(Pc)O]_n$	σ_{RT} ohm^{-1} cm^{-1}	Nondoped	3×10^{-8}	(5)
	σ (300 K) ohm^{-1} cm^{-1}	Nondoped	5.5×10^{-6}	(6)
$\{[Si(Pc)O]I_y\}_n$	σ_{RT} ohm^{-1} cm^{-1}	0.50	2×10^{-2}	(5)
		1.40	2×10^{-1}	(5)
		4.60	1×10^{-2}	(5)
$\{[Si(Pc)O](I_3)_y\}_n$	s (300 K) ohm^{-1} cm^{-1}	0.37	5.8×10^{-1}	(6)
$\{[Si(Pc)O]Br_y\}_n$	σ_{RT} ohm^{-1} cm^{-1}	1.00	6×10^{-2}	(5)
$\{[Si(Pc)O]BF_{4y}\}_n$	σ (300 K) ohm^{-1} cm^{-1}	0.00[a]	3.0×10^{-4}	(7)
		0.00[b]	2.2×10^{-6}	(7)
		0.11	3.7×10^{-3}	(6)
		0.13	3.3×10^{-3}	(7)
		0.18	2.4×10^{-2}	(6)
		0.19	1.4×10^{-2}	(7)
		0.20	5.3×10^{-2}	(6)
		0.27	2.9×10^{-2}	(7)
		0.28	6.7×10^{-2}	(6)
		0.31	9.0×10^{-2}	(6)
		0.36	1.8×10^{-1}	(7)
		0.36	8.6×10^{-2}	(6)
		0.41	1.2×10^{-1}	(7)
		0.50	1.3×10^{-1}	(7)
$\{[Si(Pc)O]TOS_y\}_n$		0.10	5.6×10^{-4}	(7)
(TOS = *p*-toluenesulfonate)		0.19	1.0×10^{-2}	(7)
		0.28	2.0×10^{-2}	(7)
		0.37	3.7×10^{-2}	(7)
		0.52	4.5×10^{-2}	(7)
		0.67	4.3×10^{-2}	(7)
$\{[Si(Pc)O]SO_{4y}\}_n$		0.040	8.5×10^{-3}	(7)
		0.095	8.8×10^{-2}	(7)
$\{[Si(Pc)O]PF_{6y}\}_n$	σ (300 K) ohm^{-1} cm^{-1}	0.08	1.3×10^{-2}	(6)
		0.18	1.7×10^{-2}	(6)
		0.20	2.3×10^{-2}	(6)
		0.32	7.8×10^{-2}	(6)
$\{[Si(Pc)O]SbF_{6y}\}_n$	σ (300 K) ohm^{-1} cm^{-1}	0.39	1.5×10^{-1}	(6)
$[Ge(Pc)O]_n$	σ_{RT} ohm^{-1} cm^{-1}	Nondoped	$<10^{-8}$	(5)
$\{[Ge(Pc)O]I-y\}_n$	σ_{RT} ohm^{-1} cm^{-1}	1.80	3×10^{-2}	(5)
		1.90	5×10^{-2}	(5)
		1.94	6×10^{-2}	(5)
		2.0	1×10^{-1}	(5)
$[Sn(Pc)O]_n$	σ_{RT} ohm^{-1} cm^{-1}	Nondoped	$< 10^{-8}$	(5)
$\{[Sn(Pc)O]I_y\}_n$	σ_{RT} ohm^{-1} cm^{-1}	1.2	1×10^{-6}	(5)
		5.5	2×10^{-4}	(5)

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POLYMER	UNITS	*y*	VALUE	REFERENCE
$\{[Fe(Pc)pyz]I_y\}_n$	σ_{RT} ohm^{-1} cm^{-1}	0[c]	7.79×10^{-8}	(8)
		0.19[d]	9.31×10^{-4}	(8)
		0.38[d]	2.58×10^{-3}	(8)
		0.77[d]	8.63×10^{-3}	(8)
		2.10[d]	7.55×10^{-3}	(8)
		2.76[d]	2.33×10^{-2}	(8)
		0.38[e]	4.60×10^{-4}	(8)
		1.49[e]	5.99×10^{-3}	(8)
		2.10[e]	1.28×10^{-1}	(8)
		2.54[e]	1.90×10^{-1}	(8)
$[Fe(Pc)tz]_n$	σ_{RT} ohm^{-1} cm^{-1}	Nondoped[f]	2×10^{-2}	(9)
$[Ru(Pc)tz]_n$		Nondoped[f]	1×10^{-2}	(9)
$[Fe(Pc)Me_2tz]_n$		Nondoped[f]	4×10^{-3}	(9)
$[Ru(Pc)(NH_2)_2tz]_n$		Nondoped[f]	4×10^{-3}	(9)
$[Ru(Pc)p\text{-}(NH_2)C_6H_4]_n$		Nondoped[f]	5×10^{-9}	(9)
$[Ru(Pc)Cl_2tz]_n$		Nondoped[f]	3×10^{-3}	(9)
$[Os(Pc)pyz]_n$		Nondoped[f]	1×10^{-6}	(9)
$[Os(Pc)tz]_n$		Nondoped[f]	1×10^{-2}	(9)
$[Fe(Me_8Pc)pyz]_n$		Nondoped[f]	3×10^{-9}	(9)
$[Fe(Me_8Pc)tz]_n$		Nondoped[f]	1×10^{-2}	(9)
$[Ru(Pc)Me_2tz]_n$		Nondoped[f]	4×10^{-3}	(9)
$[Fe(CN_4Pc)pyz]_n$		Nondoped[f]	5×10^{-9}	(9)
$[Fe(CN_4Pc)tz]_n$		Nondoped[f]	1×10^{-6}	(9)
$[Fe(2,3\text{−}Nc)pyz]_n$		Nondoped[f]	5×10^{-5}	(9)

[a] Orthorhombic. [b] Tetragonal. [c] Prepared by: $n\text{Fe(Pc)} + n(\text{pyz}) \xrightarrow{C_6H_5Cl \text{ or benzene}} [\text{Fe(Pc)(pzy)}]_n$.
[d] Prepared by: $[\text{Fe(Pc)(pyz)}]_n + (ny/2)I_2 \xrightarrow{\text{benzene}} \{[\text{Fe(Pc)(pyz)}]I_y\}_n$.
[e] Prepared by: $n[\text{Fe(Pc)(pyz)}]_n + (ny/2)I_2 \xrightarrow{CHCl_2} \{[\text{Fe(Pc)(pyz)}]I_y\}_n + n(\text{pyz})$.
[f] Room temperature, pressed pellets, 1 kbar.

Thermoelectric power[7]

Polymer	*y*	*S* (300 K)[a] (μV K^{-1})	$(\Delta S/\Delta T) \sim 300$ (mV K^{-2})	$4t$[b] (eV)
$\{[Si(Pc)O]BF_{4y}\}_n$	0.13	113		
	0.19	62.9		
	0.27	43.4	0.101	2.70
	0.36	10.5	0.134	1.16
	0.41	4.6	0.135	0.81
	0.50	0.31	0.100	0.70
$\{[Si(Pc)O]TOS_y\}_n$	0.10	284		
	0.19	114		
	0.28	82.1	0.079	4.2
	0.37	50.9	0.115	1.27
	0.52	28.2	0.109	0.63
	0.67	26.0	0.096	0.36
$\{[Si(Pc)O]SO_{4y}\}_n$	0.095	48.6	0.17	3.8

[a] S_{sample} = (Slope of voltage ∼ temp. data) $(S_{thermocouple}) + S_{gold}$.
[b] Tight-binding bandwidth derived from a fit to: $S = [2\pi^2 k_B^2 T \cos(\pi\rho/2)]/[3e(4t)\sin^2(\pi\rho/2)]$.

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Static magnetic susceptibility

Polymer	y	χ_{Pauli} [(a)] (10^{-4} emu mol^{-1})	Pauli-like spins/M(Pc)[(b)]	A (10^{-4})	α	Curie-like spins/M(Pc)[(c)]	Reference
$\{[Si(Pc)O]BF_{4y}\}_n$	0.11	0.68	0.05	135	0.82	0.10	(7)
	0.19	1.40	0.11	16	0.67	0.13	(7)
	0.26	2.39	0.19	101	0.83	0.07	(7)
	0.35	2.22	0.18	92	1.00	0.024	(7)
	0.43	2.28	0.18	90	1.00	0.024	(7)
	0.50	2.32	0.18	83	1.00	0.022	(7)
$\{[Si(Pc)O]TOS_y\}_n$	0.67	3.13	0.25	124	1.00	0.032	(7)
$\{[Si(Pc)O]SO_{4y}\}_n$	0.095	1.93	0.15	116	0.82	0.09	(7)
$\{[Si(Pc)O]BF_{4y}\}_n$	0.36	2.22	0.18	–	–	–	(6)
$\{[Si(Pc)O]PF_{6y}\}_n$	0.36	2.49	0.19	–	–	–	(6)
$\{[Si(Pc)O]SbF_{6y}\}_n$	0.36	2.22	0.18	–	–	–	(6)
$\{[Si(Pc)O](I_3)_y\}_n$	0.37	2.35	0.18	–	–	–	(6)
$\{[Ge(Pc)O](I_3)_y\}_n$	0.37	2.70	0.21	–	–	–	(6)

[(a)] For $\chi = \chi_{Pauli} + AT^{\alpha}$.
[(b)] $N_p = {}^3\chi_{Pauli}kT/Ng^2\mu_B^2S(S+1)$, where $T = 298$ K.
[(c)] $Nc = 3AT^{1-\alpha}k/Ng^2\mu_B^2S(S+1)$, where $T = 298$ K.

Unit cell dimensions

Polymer	y	Space group	Z	Cell dimensions (Å) a	b	c	Interplanar spacing (Å)	Staggering angle ϕ (degrees)	Reference
$[Si(Pc)O]_n$	–	Ibam	4	13.80	27.59	6.66	3.33	39	(5)
$[Ge(Pc)O]_n$	–	$P4/m$	1	13.27	3.53	–	3.53	0	(5)
	–	$I4/m$	2	18.76	3.57	–	3.57	0	(5)
$[Sn(Pc)O]_n$	–	$P4/m$	1	12.81	3.8	–	3.82	Probably eclipsed	(5)
$[Ga(Pc)F]_n$	–	PI		3.871	12.601	12.793	3.87	Probably eclipsed	(5)
$\{[Si(Pc)O]BF_{4y}\}_n$	0.36	$P4/mcc$	2	13.70	–	6.58	3.29	40	(6, 7)
	0.50	$P4/mcc$	2	13.96	–	6.66	–	–	(7)
$\{[Si(Pc)O]PF_{6y}\}_n$	0.36	$P4/mcc$	2	13.98	–	6.58	3.29	40	(6, 7)
	0.47	$P4/mcc$	2	14.08	–	6.63	–	–	(7)
$\{[Si(Pc)O]SbF_{6y}\}_n$	0.36	$P4/mcc$	2	14.31	–	6.58	3.29	40	(6, 7)
	0.41	$P4/mcc$	2	14.19	–	6.61	–	–	(7)
$\{[Si(Pc)O](I_3)_y\}_n$	0.37	$P4/mcc$	2	13.97	–	6.60	3.30	39	(6)
$\{[Si(Pc)O](Br_3)_y\}_n$	0.37	$P4/mcc$	2	13.97	–	6.60	3.30	39	(6)
$\{[Ge(Pc)O](I_3)_y\}_n$	0.36	$P4/mcc$	2	13.96	–	6.96	3.48	40	(6)
$\{[Si(Pc)O]TOS_y\}_n$	0.67	$P4/mcc$	2	14.39	–	6.64	–	–	(7)
$\{[Si(Pc)O]PYS_y\}_n$	0.22	$P4/mcc$	2	13.70	–	6.65	–	–	(7)
$\{[Si(Pc)O](CF_3SO_3)y\}_n$	0.55	$P4/mcc$	2	13.99	–	6.60	–	–	(7)
$\{[Si(Pc)O]SO_{4y}\}_n$	0.095	$P4/mcc$	2	13.86	–	6.67	–	–	(7)
$\{[Si(Pc)O]NFBS_y\}_n$	0.36	$P4/mcc$	2	14.37	–	6.63	–	–	(7)
$\{[Si(Pc)O]PFOS_y\}_n$	0.26	$P4/mcc$	2	13.91	–	6.61	–	–	(7)

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Other physical properties[4]

PROPERTY	POLYMER	CONDITIONS
Color	$[Si(Pc)O]_n$	Dark purple powder
Solubility	$[Si(Pc)O]_n$	Concentrated H_2SO_4 and HSO_3CH_3: 0.013 g in 25 ml concentrated H_2SO_4 at room temperature 0.020 g in 25 ml concentrated H_2SO_4 at 80C

Densities

POLYMER	y	DENSITY (G CM^{-3})		REFERENCE
		CALCULATED	FOUND	
$[Si(Pc)O]_n$	–	1.458	1.432	(4, 6)
$[Ge(Pc)O]_n$	–	1.609[a]	1.512	(4, 6)
	–	1.589[b]	–	(4, 6)
$[Sn(Pc)O]_n$	–	1.715	1.719	(4, 6)
$\{[Si(Pc)O]BF_{4y}\}_n$	0.36	1.581	1.545	(6)
$\{[Si(Pc)O]PF_{6y}\}_n$	0.36	1.573	1.563	(6)
$\{[Si(Pc)O]SbF_{6y}\}_n$	0.36	1.582	1.591	(6)
$\{[Si(Pc)O](I_3)_y\}_n$	0.37	1.802	1.744	(6)
$\{[Ge(Pc)O](I_3)_y\}_n$	0.36	1.805	1.774	(6)

[a] Space group: $P4/m$; $Z = 1$; $a = 13.27$, $c = 3.53$.
[b] Space group: $I4/m$; $Z = 2$; $a = 18.76$, $c = 3.57$.

Infrared spectroscopy[4]

POLYMER	IR SPECTRAL DATA (CM^{-1})*
$[Si(Pc)O]_n$	530(m), 575(m), 646(w), 721(vs), 759(vs), 762(w), 804(w), 869(vw), 910(s), 936(vw), 1000(bd), 1043(m), 1080(vs), 1121(vs), 1164(s), 1170(sh), 1192(w), 1289(s), 1334(vs), 1351(m), 1426(vs), 1517(s), 1596(w), 1614(m)
$[Ge(Pc)O]_n$	425(vw), 435(vw), 508(m), 572(m), 640(w), 660(vw), 725(vs), 753(m), 762(vw), 772(vw), 801(w), 865(bd), 899(s), 935(vw), 945(vw), 970(vw), 998(w), 1068(vs), 1087(vs), 1119(vs), 1162(s), 1195(w), 1284(m), 1332(vs), 1345(m), 1419(s), 1500(m), 1588(w), 1612(m)
$[Sn(Pc)O]_n$	428(w), 435(sh), 495(m), 570(m), 640(w), 660(vw), 687(vw), 716(vs), 750(s), 762(m), 769(m), 775(sh), 808(m), 825(bd), 872(w), 888(m), 950(w), 1005(vw), 1058(s), 1089(s), 1120(vs), 1168(m), 1183(w), 1263(w), 1284(m), 1293(w), 1338(vs), 1405(sh), 1580(sh), 1610(m)

*Peaks not readily assigned to M(Pc) moiety; s = strong, m = medium, w = weak, bd = broad, sh = shoulder, v = very.

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Optical spectroscopy[4]

COMPOUND	ABSORPTION MAXIMUM (NM)
$[Si(Pc)O]_n$	203, 285, 335, 625
$[Ge(Pc)O]_n$	285, 350, 645
$[Sn(Pc)O]_n$	205, 290, 365, 655, 695

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Nylon 3

JUNZO MASAMOTO

CLASS Aliphatic polyamides

STRUCTURE $[-CH_2CH_2CONH-]$

MAJOR APPLICATION Thermal stabilizer for polyoxymethylene, and stabilizer for polyacetal resin. Because of high amide concentration, nylon 3 shows properties of an excellent formaldehyde scavenger.[1]

PROPERTIES OF SPECIAL INTEREST Nylon 3 shows properties of an excellent stabilizer for polyoxymethylene. Features of nylon 3 as a stabilizer for polyoxymethylene are as follows: High thermal stability, negligible decoloration when the polymer remains for a long time in injection mold machine at its molten state, and low deposit on the mold.[1] Nylon 3 is an interesting material as an odd-numbered nylon with shortest methylene group, thus forming high glass transition temperature and high absorption of water.

OTHER POLYMER SHOWING THIS SPECIAL PROPERTIES Formaldehyde scavenger: copolyamide composed of Nylon 6, Nylon 6,6 and Nylon 6,10.

PREPARATIVE TECHNIQUES Hydrogen transfer polymerization: Acryl amide is polymerized in the presence of a strong base catalyst (e.g., *t*-BuOK). The polymerization occurs with hydrogen transfer, producing nylon 3. The polymerization is conducted using inactive solvents, such as toluene, pyridine, chlorobenzene, and *o*-dichlorobenzene from 80 to 200°C.[1–4]

The following methods were also reported for the preparation of nylon 3: anionic ring-opening polymerization of β-lactam (β-propiolactam);[5,6] ring-opening polymerization of 8-ring dilactam (1,5-diazacyclooctane-2,6-dion);[7] thermal polymerization of ethylene cyanehydrine;[8] and alternative copolymerization of carbon monoxide and ethylene imine.[9]

The polymerization method of α-amino acid to nylon 3 poly(-β-alanine) was also studied. For example, nylon 3 was synthesized from β-alanine N-carboxyanhydride (NCA), N-dithiocarbonyl ethoxycarbonyl-β-alanine and N-carbothiophenyl-β-alanine.[10–12]

The use of various active β-alanine esters for the preparation of poly(-β-alanine) was proposed.[13] The direct condensation of β-alanine to obtain nylon 3 was also reported.[14]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	71	–
Typical molecular weight range of polymer	$g\,mol^{-1}$	Light scattering	M_w = 90,000–120,000	(15)
		Light scattering	M_w = 80,000	(2)
		Viscosity	43,000	(16, 17)
		Intrinsic viscosity in 90% formic acid	54,000	(18)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
IR (characteristic absorption frequencies)	cm^{-1}	Amide VII for the extended planar zigzag conformation of the molecular chain	240	(19)
		Skeletal vibration of delta methylene $CH_2CONHCH_2$)	365	(19)
		Skeletal vibration of delta methylene NCH_2CH_2	465	(19)
		Amide VI	580	(19)
		Amide V	700	(19)
		NH asymmetric	3,400	(20)
		NH asymmetric	3,250	(20)
		$-NH\cdots C{=}O$	3,070	(20)
		$CH_2(N)$	2,927	(20)
		CH_2	2,890	(20)
		C=O amide I	1,640	(20)
		Amide II	1,530	(20)
		Amide III	1,283, 1,220	(20)
		Amide IV	1,100, 1,040, 960	(20)
		Amide V	683	(20)
Raman	cm^{-1}	Amide VI	577	(21)
		Amide V	682	
		C–CO stretch	970	
		C–C stretch	1,110	
		NH wagging	1,227	
		Amide III	1,260	
		CH_2 twisting	1,293	
		CH_2 wagging	1,367	
		CH_2–CO bending	1,426	
		CH_2 bending	1,443	
		Amide I	1,630	
		Symmetric CH_2 stretching	2,853, 2,900	
		Asymmetric CH_2 stretching	2,933	
		CH_2 stretching	2,963/2,995	
		NH stretching	3,293	
NMR	60 MHz ^1H NMR: trifluoroacetic acid at 60°C with Varian A 60			(3)
	^1H NMR: D_2O (0.5% solution) at room temperature with a Bruker Model-WH 270 spectrometer			(22)
	^{13}C NMR: FSO3H, 90.5 MHz with a Bruker WH 360 FT-NMR spectrometer			(23)
Solvents	Soluble at room temperature: formic acid, dichloroacetic acid, trifluoroacetic acid			(24)
	Soluble at 60°C: chloral hydrate			
Nonsolvents	Insoluble at room temperature: water, methanol, butanol			(25)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Mark-Houwink parameters: *K* and *a*	$K = \text{ml g}^{-1}$ a = None	0.4 mol-KCl/*l*-HCOOH, at 35°C	$K = 1.6 \times 10^{-4}$ $a = 0.50$	(26)
Huggins constants k'	–	99 wt% formic acid: 90 wt% formic acid: 80 wt% formic acid 0.4 mol-KCl/99 wt%-HCOOH 0.4 mol-KCl/80 wt%-HCOOH	0 0.4 0.5 0.4 0.5	(27)
Lattice	–	Modification I	Monoclinic Orthorhombic	(19, 28, 29) (28)
Space group	–	–	$P2_1$ C2-2	(19) (28)
Chain conformation	–	Modification I (monoclinic), II, and III	Extended chain of planar zigzag	(19)
		Monoclinic form and orthorhombic form	Both extended	(28)
Unit cell dimensions	Å	Modification I (monoclinic)	$a = 9.33$, $b = 4.78$ (fiber identity period), $c = 8.73$	(19, 29)
(19, 29)		Monoclinic	$a = 9.60$, $b = 4.78$ (fiber identity period), $c = 8.96$	(28)
(19, 29)		Orthorhombic	$a = 9.56$, $b = 4.78$ (fiber identity period), $c = 7.56$	(19, 29)
Unit cell angles	degrees	Monoclinic, modification I Monoclinic Monoclinic	$\beta = 60$ $\beta = 122.5$ $\beta = 57.5$	(19) (28) (30)
Unit cell contents	monomeric units	Monoclinic form	4	(19, 28–30)
		Orthorhombic form	4	(28)
Degree of crystallinity	%	Dielectric relaxation of nylon 3 powder	38	(31)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	g cm^{-3}	Theoretical density for modification I	1.39	(19)
		Observed density for nylon 3 drawn fiber (modification I) at 25°C	1.33	(19)
		Observed density for nylon 3 undrawn fiber (modification II) at 25°C	1.32	(19)
		Observed density for nylon 3 for modification III at 25°C	1.33	(19)
		Theoretical density for monoclinic and orthorhombic	1.36	(28)
		Observed density for nylon 3		
		Form I (monoclinic)	1.30	(28)
		Form II (orthorhombic)	1.27	(28)
Polymorphs	Modification I (monoclinic); Modification II; Modification III; Modification IV (smectic hexagonal)			(19)
	Form I (monoclinic); Form II (orthorhombic)			(28)
Glass transition temperature	K	Tan δ maximum of drawn fiber	443–453	(32)
		DTA	384	(33)
		Dielectric relaxation of nylon 3 powder	384	(31)
		20 K min^{-1}, with a Perkin Elmer DSC 4	396	(34)
		NMR method, water insoluble nylon 3 in dry state	480	(18)
Melting point	K	With decomposition, water insoluble polymer	613	(2)
		With decomposition, water soluble polymer	598	(2)
		Hot stage microscope, water insoluble nylon 3	625	(18)
Sub T_g transition	K	NMR, local motion of the methylene groups of the polymer chain in amorphous region, molecular chain approach a rigid structure in this temperature range	77–130	(18)
Tensile modulus	MPa	Drawn and wet heat-treated fiber	8,000–12,000	(32)
Tensile strength	MPa	Drawn and wet heat-treated fiber	240–360	(32)
Yield strain	%	Drawn and wet heat-treated fiber	3	(32)
Maximum extensibility	%	Drawn and wet heat-treated fiber	10–20	(32)
Dielectric constant	–	10^{-3}–10^{-7} Hz, 30°C	4.7	(31)
Dielectric loss	–	10^{-3}–10^{-7} Hz, 30°C	10^{-2}–10^{-1}	(31)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Decomposition temperature	K	50% weight loss, 2°C min^{-1}, in air	608–613	(31)
Water absorption	%	60% RH, 25°C	7	(1)
Important Patents	U.S. Patent 4,855,365 U.S. Patent 5,015,707, assigned to Asahi Chemical			
Availability	Not commercially available (only used inside Asahi Chemical Industry Company Ltd., 1-1-2, Yuraku-cho, Chiyoda-ku, Tokyo, 100 Japan)			

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Nylon 4,6

DINESH V. PATWARDHAN

TRADE NAMES Stanyl (DSM); TW300 (dry, unfilled Stanyl); TW241F10 (dry, 50% glass fiber filled Stanyl). Approximately 50 other varieties of filled or unfilled Stanyl are available.

CA NUMBER 50327-22-5[1]

CLASS Aliphatic polyamides; Nylons

STRUCTURE $H{-}(HN{-}(CH_2)_4{-}HN{-}CO{-}(CH_2)_4{-}CO)_n{-}OH$

PREPARATIVE TECHNIQUES Nylon 4,6 is polymerized from 1,4-diaminobutane and adipic acid; 1,4-diaminobutane is prepared separately by reacting acrylonitrile and HCN followed by hydrogenation. The first step in polymer formation involves condensing the two monomers, 1,4-diaminobutane and adipic acid, to give a low molecular weight pre-polymer. This is done at lower temperature (200°C) to avoid formation of cyclics by the amine. In a separate step, this pre-polymer is molded into uniform cylindrical pellets and heated to about 250°C in an atmosphere of nitrogen and steam. The use of pre-formed pellets is important for uniform rate of solid-state polymerization and thus the degree of polymerization. These pellets are especially important for nylon 4,6 because transamidation, which leads to uniform molecular weight, cannot be performed on the final melt due to the sensitivity of nylon 4,6 to thermal degradation. The typical molecular weight range of nylon 4,6 thus obtained is 30,000 g mol^{-1} with polydispersity of 1.15.[1–4]

MAJOR APPLICATIONS Nylon 4,6 is often blended with glass fiber or polytetrafluoroethylene and is used in underhood automotive parts, gears, electrical parts, and bearings.[5]

PROPERTIES OF SPECIAL INTEREST Distribution of methylene moieties in nylon 4,6 exists in regular groups of four. This high order leads to higher crystallinity and a faster rate of crystallization compared with other polyamides such as nylon 6,6 or nylon 6. Nylon 4,6 therefore has higher tensile strength, heat deflection, and tenacity, which makes it a better high-temperature engineering plastic compared with more common polyamides. On the other hand, high moisture regain is a significant drawback.[1,3]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Specific gravity/density	—	23°C, dry, unfilled (TW300)	1.18	(6)
Melting point	K	Dry, unfilled (TW300)	563	(6)
Specific heat	btu/lb-F	—	0.5	(5)
Solvent	—	Dry, unfilled (TW300)	95% formic acid	(4)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
IR (characteristic absorption frequencies)	cm^{-1}	Obtained on thin films from formic acid solution		(4)
		N–H	3,300 (vs); 3,070 (m)	
		$C–H_2$	2,945 (s); 2,870 (m)	
		Amide I–VI	1,638 (vvs); 1,540 (vvs); 1,280 (m); 940 (w); 730 (sh); 690 (s,b); 575 (m); 520 (w)	
NMR	ppm	Deuterated formic acid as the solvent		(7)
		^{1}H	1.57; 1.66; 2.37; 3.27	
		^{13}C	25.19; 25.95; 35.46; 39.65	
Crystalline state properties				(8)
Crystal system	–	–	Monoclinic	
Unit cell dimensions	nm	–	$a = 0.49$, $b = 0.53$, $c = 1.48$	
Cell angles	Degrees	–	$\alpha = 51$, $\beta = 77$, $\gamma = 62$	
Heat of fusion	$kJ\,mol^{-1}$	Sample quenched and annealed for 5 min at 279°C	15.1	(4)
Tensile modulus	MPa	Dry, unfilled (TW300)	3,000	(5)
		Dry, filled (TW241F10)	16,000	(9)
Tensile strength at break	MPa	Dry, unfilled (TW300)	99.31	(5)
Tensile strength at yield	MPa	Dry, unfilled (TW300)	79.31	(5)
		Dry, filled (TW241F10)	234.5	(9)
Yield stress	MPa	Dry, unfilled (TW300)	95	(6)
Elongation at break	%	Dry, unfilled (TW300)	30	(5)
Flexural modus	MPa	Dry, unfilled (TW300)	3,100	(6)
		Dry, filled (TW241F10)	14,000	(9)
Flexural strength at yield	MPa	Dry, unfilled (TW300)	149.6	(5)
		Dry, filled (TW241F10)	350	(9)
Impact strength	ft-lb/in	Izod, 73°F, dry, unfilled	1.8	(5)
		Dry, filled (TW241F10)	2.2	(9)
Hardness	Shore D	Durameter	85	(5)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Poisson ration	–	–	0.37	(5)
Dielectric constant ε'	–	1 kHz	3.83	(5)
Resistivity	ohms cm	–	5×10^{14}	(5)
Surface resistivity	ohms	–	8×10^{15}	(5)
Thermal conductivity	btu-in/hr-ft^2-F	–	2	(5)
Water absorption	%	50% relative humidity	3	(6)
Vicat softening temperature	K	–	560.8	(5)
Distortion temperature	K	–	433	(10)
Cost	US\$ kg^{-1}	Dry, unfilled, 1994 price	6.5	(2)
Supplier	DSM Engineering Plastics, P.O. Box 3333, 2267 West Mill Road, Evansville, Indiana 47732, USA			(9)

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Nylon 6

PAUL G. GALANTY

ACRONYM, ALTERNATIVE NAME, TRADE NAMES PA-6, poly-ε-caproamide, Capron®, Ultramid®, Nylatron®

CLASS Aliphatic polyamides

STRUCTURE $[-NH(CH_2)_5CO-]$

MAJOR APPLICATIONS Gears, fittings, and bearings. Electrical switches, bobbins, and connectors. Food packaging film. Monofilament for weed trimmers and fishing line. Blow and roto-molded containers. Wire and cable jacketing. Power tool housings, wheelchair wheels, automotive cooling fans, and other underhood parts.

PROPERTIES OF SPECIAL INTEREST Excellent load bearing (strength and stiffness) capability at elevated temperatures. Good chemical and abrasion resistance. Low coefficient of friction. Toughness and impact resistance.

PREPARATIVE TECHNIQUES (a) Hydrolytic polymerization of ε-caprolactam;[1] temperature = 250–260°C; pressure cycle for hydrolysis and addition; vacuum cycle for accelerated rate condensation. (b) Solid state polymerization for very high molecular weight;[1] temperature = 140–170°C (higher temperature causes discoloration); high vacuum to reach target molecular weight; nitrogen purge at atmospheric pressure is a costly alternative.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Monomer	–	–	ε-Caprolactam	(2)
Molecular mass	$g\,mol^{-1}$	–	113.16	
Melting point	K	–	342.2	
Boiling point	K	–	543	
Bulk density	$g\,cm^{-3}$	–	0.6–0.7	
Polymerization heats of reaction	$kcal\,mol^{-1}$	Hydrolysis	2.1	(3)
		Addition	−4	
		Condensation	−6.1	
Repeat unit	$[-NH(CH_2)_5CO-]$			(4)
Molecular mass range	$g\,mol^{-1}$	Typical as sold	1.8–5.2 ($\times 10^4$)	(3)
		Solid state	$\sim 1 \times 10^5$	
Typical polydispersity index	–	–	1.9–2.0	(3)
IR (characteristic absorption frequencies)	cm^{-1}	Assignment		(5)
		N–H hydrogen-bonded stretch	3,300	
		C=O amide I stretch	1,640	
		C–N amide II stretch	1,545	

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Chemical resistance[6]

Chemical	Temp. (°C)	Conc. (%)	Rating			
			Excellent	Good	Poor	Severe attack
Acetone	23	100	✓			
Benzene	23	100	✓			
Ethylene glycol/water	23	50		✓		
Ethylene glycol/water	120	50				✓
Formic acid	23	90				✓
Gasoline	100	100	✓			
Gasoline/methanol (15%)	23	15			✓	
Hydrochloric acid	23	10				✓
Potassium hydroxide	23	10		✓		
Potassium hydroxide	60	20			✓	
Trichloroethylene	23	100		✓		
Water	Up to 50	100		✓		
Water (steam)	100–150	100				✓

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Lattice	—	—	Monoclinic	(7)
Unit cell dimensions	nm	α structure	$a = 0.956$, $b = 1.724$, $c = 0.801$	(7)
		γ structure	$a = 0.933$, $b = 1.688$, $c = 0.478$	
Unit cell angles	Degrees	α structure	67.5	(7)
		γ structure	121	
Unit cell contents	—	α structure	4	(7)
		γ structure	4	
Heat of fusion	$J\,g^{-1}$	Calorimetry	188	(8)
Density	$g\,cm^{-3}$	ASTM D-792; dry as molded	1.13	(9)
Degree of crystallinity	%	Typical molded	50	(10)
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ $a =$ None	In 85% formic acid; 25°C	$K = 0.023$ $a = 0.82$	(11)
Polymorphs	—	—	α, γ	(7)
Refractive index	—	At thickness < 0.5 mm; molded, undrawn	1.53	(12)
Glass transition temperature	K	DSC	320–330	(13)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melting point	K	ASTM D-789; Fisher-Johns	493	(9)
Specific heat	$J\,g^{-1}\,K^{-1}$	Neat, 0°C	1.38	(14)
		Neat, 120°C	2.30	
		Neat, 160°C	2.68	
Thermal expansion coefficient	$mm\ (mm\ K)^{-1}$	ASTM D-696		(9)
		Neat resin	8.30×10^{-4}	
		33% glass fiber	3.80×10^{-4}	
Deflection temperature under load	K	ASTM D-648		(9)
		Neat resin		
		Load = 1.80 MPa	338	
		Load = 0.45 MPa	438	
		33% glass fiber		
		Load = 1.80 MPa	483	
		Load = 0.45 MPa	493	
Tensile strength, yield	MPa	ASTM D-638		(9)
		Neat resin		
		DAM, 23°C*	79	
		DAM, 121°C	21	
		50% RH, 23°C*	36	
		33% glass fiber		
		DAM, 23°C	200	
		DAM, 121°C	83	
		50% RH, 23°C	127	
Tensile elongation, yield	%	ASTM D-638		(9)
		Neat resin		
		DAM, 23°C	7	
		DAM, 121°C	15	
		50% RH, 23°C	16	
		33% glass fiber		
		DAM, 23°C	3	
		DAM, 121°C	7	
		50% RH, 23°C	6	
Tensile elongation, ultimate	%	ASTM D-638		(9)
		Neat resin		
		DAM, 23°C	70	
		DAM, 121°C	>300	
		50% RH, 23°C	260	
		33% glass fiber		
		DAM, 23°C	3	
		DAM, 121°C	7	
		50% RH, 23°C	6	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Flexural strength	MPa	ASTM D-790		(9)
		Neat resin		
		DAM, 23°C	108	
		DAM, 121°C	17	
		50% RH, 23°C	35	
		33% glass fiber		
		DAM, 23°C	276	
		DAM, 121°C	112	
		50% RH, 23°C	179	
Flexural modulus	MPa	ASTM D-790		(9)
		Neat resin		
		DAM, 23°C	2,829	
		DAM, 121°C	304	
		50% RH, 23°C	738	
		33% glass fiber		
		DAM, 23°C	9,384	
		DAM, 121°C	3,319	
		50% RH, 23°C	5,127	
Notched Izod impact strength	$J m^{-1}$	ASTM D-256		(9)
		Neat resin		
		DAM, 23°C	53	
		50% RH, 23°C	NB	
		33% glass fiber		
		DAM, 23°C	117	
		50% RH, 23°C	235	
Hardness, Rockwell	R scale	ASTM D-785; DAM, 23°C		(9)
		Neat resin	119	
		33% glass fiber	121	
Abrasion resistance	mg $kcycles^{-1}$	ASTM D-1044, Taber; DAM, 23°C		(15)
		Neat resin	9	
		33% glass fiber	30	
Volume resistivity	ohm cm	ASTM D-257; DAM, 23°C		(9)
		Neat resin	1.00×10^{14}	
		33% glass fiber	1.00×10^{15}	
Surface resistivity	ohms	ASTM D-257; DAM, 23°C		(9)
		Neat resin	1.00×10^{15}	
		33% glass fiber	1.00×10^{15}	
Dielectric constant	–	ASTM D-150; DAM, 23°C, 1 MHz; 33% glass fiber	3.80	(9)
Dissipation factor	–	ASTM D-150; DAM, 23°C, 1 MHz; 33% glass fiber	0.022	(9)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric strength, short time	$kV\,mm^{-1}$	ASTM D-149; DAM, 23°C, 3.2 mm		(9)
		Neat resin	460	
		33% glass fiber	560	
Thermal conductivity	$W\,(m\,K)^{-1}$	–	0.23	(16)
Coefficient of friction	–	ASTM D-1894, polymer to steel		(17)
		Neat resin		
		Static	0.24	
		Dynamic	0.16	
		33% glass fiber		
		Static	0.25	
		Dynamic	0.16	
Thermal index ratings	K	UL-746B; 60,000-h half-life at indicated temperature; 3.2 mm		(9)
		Neat resin		
		Mechanical	378	
		Impact	378	
		Electrical	403	
		33% glass fiber		
		Mechanical	413	
		Impact	393	
		Electrical	413	
Moisture absorption	%	ASTM D-570; 23°C		(9)
		Neat resin		
		50% RH equilibrium	2.7	
		Saturation	9.5	
		33% glass fiber		
		50% RH equilibrium	1.9	
		Saturation	6.7	
Flammability ratings		UL-94; 3.2 mm		(9)
		Neat resin	V-2	
		33% glass fiber	HB	
Price	US\$ kg^{-1}	Commercial quantities of 2–5 $(\times 10^5)\,kg\,yr^{-1}$		(18)
		Neat resin	0.66–0.68	
		33% glass fiber	0.68–0.70	
Major suppliers	AlliedSignal, Morristown, New Jersey BASF, Mt. Olive, New Jersey Bayer, Pittsburgh, Pennsylvania Custom Resins, Henderson, Kentucky DuPont, Wilmington, Delaware Nylatech, Manchester, New Hampshire			

*DAM = tested dry as molded; 50% RH = tested after equilibration in a 50% RH, 23°C room.

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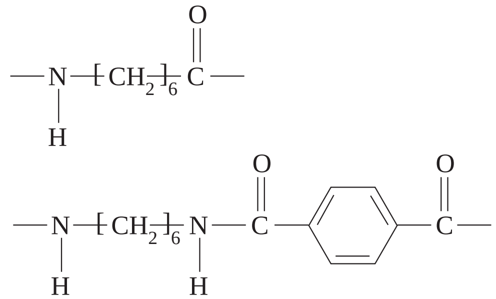
Nylon 6 copolymer

SHAW LING HSU

TRADE NAME, ALTERNATIVE NAMES Ultramid T (BASF), nylon 6/6T, polyphthalamide

CLASS Aromatic polyamides; aromatic nylon

STRUCTURE These aromatic nylons consist of aliphatic and aromatic building blocks incorporating the repeat units of nylon 6—poly(caprolactam)—and nylon 6T—poly(hexamethylene terephthalamide). Because of this composition, Ultramid T resins are often designated as nylon 6/6T materials. The basic structure is nylon 6/6T, with a majority component of nylon 6.



PROPERTIES OF SPECIAL INTEREST Extremely high melting temperature can be achieved by adjusting the relative amount of the aromatic component. Good mechanical properties at elevated temperatures. Good resistance to chemicals. Good dielectric properties. Dimensional stability in the presence of moisture. Low moisture absorption, good impact resistance, good dielectric properties, good resistance to chemicals, easy to process.

MAJOR APPLICATIONS High-temperature applications, automobile parts (e.g., radiator, ventilation, and fuel supply systems), electronics housings, plug and socket connectors, printed circuit boards, tennis rackets, golf clubs.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
NMR*	ppm	Range for amide proton peaks	6–7	(1)
		Range for methylene proton peaks	1–4	
IR (characteristic absorption frequencies)	cm^{-1}	Overall, the infrared spectrum greatly resembles those found for other polyamides. The principal spectroscopic features can be definitively assigned.		
		N–H stretching	3,305	(2, 10)
		Amide I	1,627	(2, 10)
		Amide II	1,545	(2, 10)
		Range for symmetric and asymmetric methylene stretching vibrations	3,000	(3–7, 9–15)
		Methylene bending vibrations	1,400	—

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
IR (characteristic absorption frequencies)	cm^{-1}	Other specific spectroscopic features can be linked to the presence of the nylon 6T component		(16, 17)
		Vibrations assignable to para-disubsitituted aromatic units	862, 1,019, ~1,300,[†] 1,498	(3, 8, 18)
Melting tempuratue[‡]	K	–	583–613	(20, 21)
Glass transition temperature	K	–	473	(21)
Degradation of aromatic polyamides	Plasma treatment can modify aromatic nylons reducing the concentration of amide units relative to that in untreated nylon 6,6 copolymer. When these polyamides are dissolved in acidic solution, the polyamid is gradually degraded.			(22)
Density	$g\,cm^{-3}$	–	1.18	(20)
Linear thermal expansion coefficient	%	60°C	0.2	(20)
Tensile modulus	MPa	Dry and moist	3,200	(20)
Tensile strength	MPa	Dry Moist	100 90	(20)
Heat deflection temperature	K	At 624 psi	473	(20)
Dielectric constant	–	1 MHz	4.0	(20)
Moisture absorption	%	23°C, saturation	7	(21)
		23°C, 50% RH	1.8	(20)
Solvents	Hexafluoroisopropanol (HFIP)			(22)

*Both assignments fall into the range of peak positions listed for these groups in standard NMR tables.
†Broad features.
‡A broad melting behavior starts at approximately 483 K and ends at approximately 563 K. These trends are consistent with the melting behaviors reported for nylon 6/6T copolymers.[19]

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Nylon 6,6

BRENT D. VIERS

COMMON NAME Poly(hexamethylene adipamide)

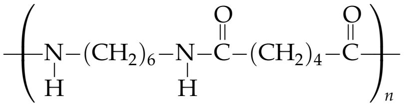
IUPAC NOMENCLATURE Poly[imino(1,6-dioxohexamethylene) imnohexamethylene], poly[iminoadipolyiminohexamethylene]

TRADE NAMES Zytel (DuPont), Maranyl (ICI), Ultramid A (BASF)

CAS REGISTRY NUMBERS 32131-17-2

CLASS Aliphatic polyamides

STRUCTURE



MAJOR APPLICATIONS Gear teeth, pinions, ball bearing cages, switch parts, spools, electro-insulating parts; semifinished products, pipes, profiles; machine parts, parts subject to wear such as friction bearings, roller bearing cages, engine parts, water pump impellers, and also parts of door locks; fan and blower wheels, parts of housings, fuel filters, clips, chain tension rails; sliding bearings for swivel chairs and folding tables, sliding feet and fittings, connecting parts in furniture making; patio and party furniture.

PROPERTIES OF SPECIAL INTEREST High mechanical strength, great rigidity, good deep-drawing behavior, good dimensional stability under heat, good toughness even at low temperatures, favorable tribological properties, good resistance to chemicals, very good electro-insulating properties, good dimensional stability, rapid processing. Relatively high T_m and T_g for aliphatic polyamides (used in synthetic fibers; can be toughened as resin).

OTHER POLYMERS SHOWING THIS SPECIAL PROPERTY Poly(ε-caprolactam) (Nylon 6). (See also the entry on *Nylon 6* in this handbook.)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Type of polymerization	—	Interfacial, melt	Condensation between hexamethylene diamine and adipic acid	—
Enthalpy of reaction $-\Delta H_a$	$kJ\,mol^{-1}$	Decrease in temperature shifts equilibrium to higher molecular weight	25–29 (average) 42–46 (limit)	(1)
Side products	1–2% of cyclic oligomers (14 membered ring)			(1)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Kinetic parameters	—	Second order kinetics, not accelerated by catalysts	Conversion <90%	(2, 3)
		Third order kinetics, carboxyl catalyzed, low water	Conversion >90%	(1, 4)
Typical comonomers	—	Aliphatic amines	Heptamethylene diamine, octamethylene diamine, decamethylene diamine, cyclohexyl diamine	—
		Aliphatic diacids (sometimes diacid chlorides)	Sebacic acid, undecanedioic acid, suberic acid	
		Aromatic amines	*p*-Xylenediamine	
		Aromatic diacids/diacid chlorides	Terephthalic acid, phenylenedipropionic acid	
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	226.3	—
Degree of branching	Can be controlled by controlled copolymerization of polyfunctional amines/acids			—
Typical molecular weight range of polymer	$g\,mol^{-1}$	High conversion ($p > 0.99$) (lowered by monofunctional end-blockers)	12,000–20,000	(1)
Typical polydispersity index (M_w/M_n)	—	Most probable	2 (expected)	(1)
		Undergoes amide interchange reactions (broadened by incorporation of multifunctional units)	1.7–2.1 (by GPC)	
Typical viscosity averages	—	Relative viscosity: 8.4% solution in 90% formic acid	$\eta_r = 30–70$	—
		Inherent viscosity: $0.5\,g/100\,cm^3$ in *m*-cresol	$\eta_{onh} = 1\,dl\,g^{-1}$	
IR (characteristic absorption frequencies)	cm^{-1}	NH wag (broad)	700	(5, 6)
		CH_2 rock	722	
		N−C=O skeletal vibration	1,170	
		N−C=O skeletal vibration	1,200	
		CH_2 wag	1,370	
		CH_2 symmetric scissors deformation (CH_2 next to C=O)	1,420	
		CH_2 symmetric scissors deformation (CH_2 next to N)	1,440	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
IR (characteristic absorption frequencies)	cm^{-1}	CH_2 symmetric scissors deformation	1,460	(5, 6)
		NH bend/C–N stretch	1,540	
		Amide C=O stretch	1,640	
		CH_2 symmetric stretch	2,860	
		CH_2 asymmetric stretch	2,920	
		2× NH bend (1,540) overtone	3,100	
		NH stretch	3,300	
NMR	s^{-1}	^{13}C NMR T_1 relaxation times		(7)
		Amorphous	1.37	
		Meso	9.2	
		Crystalline	82.5	
Thermal expansion coefficients	K^{-1} ($\times 10^{-4}$)	Zytel ASTM D 696	0.81	(8)
		Crystalline, volumetric 20°C	2.8	(9)
		Linear crystalline, 20°C	7–10	(10)
		Linear crystalline, 100°C	10–14	(10)
		Triclinic, α_a	2.1	(11)
		Triclinic, α_c	22.0	(11)
Compressibility coefficients	$(MPa)^{-1}$ ($\times 10^{-6}$)	Pressure/temperature dependence		
		50 MPa, 20°C	62	(12)
		100 MPa, 20°C	58	(12)
		150 MPa, 20°C	54	(12)
		300 MPa, 20°C	50	(12)
		50 MPa, 120°C	125	(12)
		100 MPa, 120°C	115	(12)
		150 MPa, 120°C	95	(12)
		300 MPa, 120°C	75	(12)
		>100 MPa, 200°C	>300	(13)
Molar volume	$cm^3\ mol^{-1}$	20°C, nylon rods	193	(9)
		20°C, amorphous	207.5	(14)
		20°C, amorhous group contribution calculation	208.3	(14)
Density (amorphous)	$g\ cm^{-3}$	Zytel ASTM D 792, 23°C	1.14	–
Solvents	Room temperature: trifluoroethanol, trichloroethanol, phenols, chloral hydrate, formic acid, chloro-acetic acid, HF, HCl, methanol, H_2SO_4, phosphoric acid, benzyl alcohol, ethylene chlorohydrin, 1,3 chloropropanol, 2-butene-1,4,diol., diethylene glycol, acetic acid, formamide, DMSO			–
Nonsolvents	Hydrocarbons, aliphatic alcohols, chloroform, diethyl ether, aliphatic ketones, esters			–

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Chemical resistances	Acid resistance: limited; attacked by strong acids; general order of resistance nylon 6,12 > nylon 6,6 > copolymers or nylon 6 Base resistance: Excellent at room temperature; attacked by strong bases at elevated temperatures Solvent resistance: generally excellent; some absorption of such polar solvents as water, alcohols, and certain halogenated hydrocarbons causing plasticization and dimension changes			(8)
Solubility parameter	$(MPa)^{1/2}$	δ	27.8	(15)
			24.02	(16)
			22.87	(17)
		Dispersive component δ_D	18.62	(16, 17)
		Polar component δ_P	5.11	(16)
		Hydrogen bonding component δ_H	14.12	(17)
			12.28	(16)
Theta temperature Θ	K	Carbon tetrachloride/*m*-cresol/ cyclohexane	293	(18)
		Formic acid/KCl/H_2O	298	(19, 20)
Second virial coefficient A_2	$mol\,cm^3\,g^{-2}$ $(\times 10^{-4})$	*m*-Cresol, 60°C, $M_n = 18{,}000$	183	(21)
		Formic acid (90%), 25°C, $M_n = 18{,}000$	840	(22)
		Formic acid (90%)/0.2–2.5 M KCl, 25°C, $M_n = 31{,}000$		(20)
		At 0.2 M KCl	59.2	
		At 2.5 M KCl	7.0	
		Formic acid (90%)/2.3 M KCl, 25°C, $M_n = 31{,}000$	0	(20)
		Formic acid (82.5–40%), 2 M KCl, 25°C, $M_n = 31{,}000$		(20)
		At 82.5%	−9.4	
		At 40%	36.5	
		Formic acid (90%), 2 M KCl, $2{,}000 < M_n < 52{,}000$		(18)
		At 2,000 M_n	312	
		At 52,000 M_n	10.1	
		Formic acid (75–98%), 0.5 M NaHCOO, 2,2,3,3-tetrafluoropropanol, 25°C, $M_n = 32{,}000$	1.0–4.0	(23)
		2,2,3,3-tetrafluoropropanol, 0.1 M sodium trifluroacetate, 25°C, $M_n = 62{,}000$	57.1	(24)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Fractionation	—	Fractional precipitation	*m*-Cresol/cyclohexane	(25, 26)
			Phenol/H_2O	(27)
		Turbitimetric titration	*m*-Cresol/cyclohexane	(28)
			m-Cresol/*n*-heptane	(29)
		Chromatography	Methylene chloride	(30)
		Gel permeation	Hexafluoroisopropanol	(31)
		Partition chromatography, 20°C	Formic acid/H_2O (88%)	(32)
		Sedimentation gradient: ultracentrifugation	Carbon tetrachloride/ *m*-cresol/cyclohexane	(19)
		Continuous immiscible liquid distribution	Phenol/water	(33)
Mark-Houwink parameters: K and a	$K = \text{ml g}^{-1}$ a = None	*o*-Chlorophenol, 25°C, $14{,}000 < M_n < 50{,}000$	$K = 168$, $a = 0.62$	(34)
		m-Cresol, 25°C, $14{,}000 < M_n < 50{,}000$	$K = 240$, $a = 0.61$	(34)
		m-Cresol, 25°C, $150 < M_n < 50{,}000$	$[\eta] = 0.5 + 0.0353M^{0.792}$	(18)
		Dichloroactetic acid, 25°C, $150 < M_n < 50{,}000$	$[\eta] = 0.5 + 0.0352M^{0.551}$	(18)
		2,2,3,3-Tetrafluoropropanol/ CF_3COONa (0.1 M), 25°C, $14{,}000 < M_n < 50{,}000$	$K = 114$, $a = 0.66$	(34)
		Aqueous HCOOH (90 vol%), 25°C		
		$6{,}000 < M_n < 65{,}000$	$K = 35.3$, $a = 0.786$	(34)
		$5{,}000 < M_n < 25{,}000$	$K = 110$, $a = 0.72$	(27)
		$14{,}000 < M_n < 50{,}000$	$[\eta] = 2.5 + 0.0132M^{0.873}$	(18)
		HCOOH (90%)/HCOONa (0.1 M), 25°C		
		$10{,}000 < M_n < 50{,}000$	$K = 32.8$, $a = 0.74$	(34)
		$14{,}000 < M_n < 50{,}000$	$K = 87.7$, $a = 0.65$	(34)
		$150 < M_n < 50{,}000$	$[\eta] = 1.0 + 0.0516M^{0.687}$	(18)
		HCOOH (90%)/KCl (2.3 M), 25°C		
		$14{,}000 < M_n < 50{,}000$	$K = 227$, $a = 0.50$ (θ)	(34)
		$150 < M_n < 50{,}000$	$K = 253$, $a = 0.50$ (θ)	(18)
		H_2SO_4 (95%), 25°C, $150 < M_n < 50{,}000$	$[\eta] = 2.5 + 0.0249M^{0.832}$	(18)
		H_2SO_4 (96%), 25°C, $14{,}000 < M_n < 50{,}000$	$K = 115$, $a = 0.67$	(34)
		Melt polymer, high molecular weight	$a = 3.5$	(35, 36)
Huggins constants: k_H	—	Formic acid, 25°C		(37)
		$[\eta] = 83\ \text{ml g}^{-1}$	0.20	
		$[\eta] = 100\ \text{ml g}^{-1}$	0.22 ± 0.01	
		$[\eta] = 120\ \text{ml g}^{-1}$	0.24 ± 0.02	
		$[\eta] = 140\ \text{ml g}^{-1}$	0.27 ± 0.02	
		$[\eta] = 160\ \text{ml g}^{-1}$	0.27 ± 0.02	
		$[\eta] = 180\ \text{ml g}^{-1}$	0.28 ± 0.02	
		$[\eta] = 200\ \text{ml g}^{-1}$	0.29 ± 0.01	

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PROPERTY	UNITS	CONDITIONS	VALUE			REFERENCE
Schulz-Bakke coefficients	—	Formic acid, 25°C				(37)
k_{SB}		$[\eta] = 83\,ml\,g^{-1}$	0.20			
		$[\eta] = 100\,ml\,g^{-1}$	0.22 ± 0.02			
		$[\eta] = 120\,ml\,g^{-1}$	0.24 ± 0.02			
		$[\eta] = 140\,ml\,g^{-1}$	0.26 ± 0.02			
		$[\eta] = 200\,ml\,g^{-1}$	0.28 ± 0.01			
Characteristic ratio $\langle r^2 \rangle_0/nl^2$	—	HCOOH (90%), 25°C	5.3			(25, 27)
		HCOOH (90%)/KCl 2.3 M, 25°C	6.85			(22)
			5.95			(38, 39)
End-to-end distance $r_0/M^{1/2}$	nm ($\times 10^{-4}$)	HCOOH (90%), 25°C	890 ± 40			(25, 27)
		HCOOH (90%)/KCl 2.3 M, 25°C	1,010			(22)
			935			(38, 39)
Lattice (monoclinic, etc.)	—	—	(α) I: triclinic			—
			(α) I: monoclinic			
			(α) II: triclinic			
			(β) triclinic			
			(high temperature) triclinic (170°C)			
Space group	—	—	CI-1			—
Chain conformation (ρ_n of helix)	—	—	14*1/1			—
Unit cell dimensions	Å		*a*	*b*	*c*	
		α I: monoclinic	15.7	10.5	17.3	(40)
		α I: triclinic	4.9	5.4	17.2	(41)
			5.00	4.17	17.3	(42)
			4.87	5.26	17.15	(43)
			4.97	5.47	17.29	(44)
		α II: triclinic	4.95	5.45	17.12	(44)
		β triclinic	4.9	8.0	17.2	(45)
		High temperature (170°C)	5	5.9	16.23	(46)
Unit cell angles	Degrees		α	β	γ	
		α I: monoclinic	—	73	—	(40)
		α I: triclinic	48	77	63	(41)
			81	76	63	(42)
			50	76	64	(43)
			48	77	62	(44)
		α II: triclinic	52	80	63	(44)
		β triclinic	90	77	67	(45)
		High temperature	57	80	60	(46)

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PROPERTY	UNITS	CONDITIONS		VALUE		REFERENCE
Unit cell contents (number of repeat units)	–	α I: monoclinic		9		(40)
		α I: triclinic		1		(42–44)
		α II: triclinic		1		(44)
		β triclinic		2		(45)
		High temperature		1		(46)
Bragg spacings	–	*hkl*	*d*-value (nm)	2θ (degrees)	Relative intensity	(45)
		002	0.641	13.83	w	
		100, 010, 110	0.390	22.96	vvs	
		015	0.335	26.65	w	
		110, 210	0.236	38.12	s	
		017, 127	0.233	38.69	w	
		117, 027	0.218	41.37	w	
		117, 227	0.194	46.71	w	
		020, 220	0.183	49.70	s	
Degree of crystallinity	As shown	General range		40–60%		(1)
		General equation based on density		$\alpha = 830–(900/\rho)\%$		(10)
		IR determination		Crystalline = 852 cm^{-1} Amorphous = 1,140 cm^{-1}		(1)
Heat of fusion	kJ mol^{-1}	α I triclinic		46.5		(47)
				40		(47)
				36.8		(48)
				68		(48)
				58		(48)
				46.9		(49)
				53.2		(44)
		α II triclinic		43.4		(44)
				41.9		(50)
Heat of fusion (per repeat unit)	J g^{-1}	α II triclinic		191.9		(44)
Entropy of fusion	J K^{-1} mol^{-1}	–		83–86		(10)
				79.9		(44)
Density (crystalline)	g cm^{-3}	α I triclinic		1.220		(40)
				1.24		(41)
				1.241		(42)
				1.225		(43)
				1.204		(44)
		α II triclinic		1.152		(44)
				1.165		(45)
		β, triclinic		1.25		(46)
		High temperature (170°C) triclinic		1.10		(5)
		Crystalline molded		1.09		(51)
				1.13–1.145		(51)

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Density (amorphous)	$g\,cm^{-3}$	*a* I triclinic			1.09	(52)
					1.12	(53)
					1.069	(54)
					1.095	(50)
		a II triclinic			1.095	(44)
		b, triclinic			1.09	(53)
		Amorphous molded			0.989	(51)
		Melt, 270°C			1.248	(5)
Crystal modulus	dynes cm^{-2}	α 1			175×10^4	(7)
Polymorphs (listing)	–	–			α I, α II, β, high temperature	–
Crystal growth activation energy	$kJ\,mol^{-1}$	–			64.5	(10)
Maximum crystallization rate	–	150°C			–	(7)
Growth rate (T_f = fusion temperature; T_c = crystallization temperature)	$\mu m\,s^{-1}$	Maximum linear growth			20	(51)
	$nm\,s^{-1}$	$M_n \times 10^3$	T_f (°C)	T_c (°C)		
		11.6	295	241	166.7	(55)
			295	247	58.35	(55)
			295	250	13.84	(55)
			295	252	10.50	(55)
			285	247	66.08	(55)
			262 (10 min)	251	14.21 (negative spherulites)	(56)
				256	83.4	(56)
				257	13.3	(57)
				259	9.17	(57)
				261	6.67	(57)
				263	4.17	(57)
				265	2.50	(57)
		12.9	300	246	106.7	(58)
			(30 min)	248	56.34	(58)
				253	10.84	(58)
		13.7	300	141	13,502.7	(59)
			(30 s)	160	13,669.4	(59)
				180	12,119.1	(59)
				199	8,901.8	(59)
				215	5,167.7	(59)
				230	2,117.1	(59)
				234	1,530.3	(59)
				237	920.18	(59)
				239.5	765.15	(59)
				241	471.76	(59)
				244	368.40	(59)

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Growth rate (T_f = fusion temperature; T_c = crystallization temperature)	nm s^{-1}	$M_n \times 10^3$	T_f (°C)	T_c (°C)		
		14.6	280	241.5	283.39	(58)
				243	230.05	(58)
				245	180.86	(58)
				248	33.685	(58)
				252	14.66	(58)
			300	241.5	204.4	(58)
				243	175.0	(58)
				245	128.3	(58)
				248	58.34	(58)
		14.6	300	252	$G = 5.501$	(60)
			315	241.5	280.0	(60)
				243	168.4	(60)
				245	113.4	(60)
				248	56.68	(60)
				252	6.335	(60)
		25.5 (M_w)		50	3,650.7 (positive spherulites)	(60)
				100	4,706.6	(60)
				142	6,751.3	(60)
				160	6,101.2	(60)
				178	5,201.0	(60)
				198	3,700.7	(60)
				200	12,900.6	(60)
				228	466.7	(60)
		25.5	300	180	11,435.6 (positive spherulites)	(60)
				200	7,951.5	(60)
				211	5,284	(60)
				220	2,733.8	(60)
				230	1,615.3	(60)
				235.5	680.13	(60)
				240	483.4	(60)
Hoffman-Lauritzen theory constants						(55)
Growth rate constant G_0	cm s^{-1}	–			1.55×10^3	
Diffusion activation energy U^*	cal mol^{-1}	–			167	
Chain dimensions	Å	–			$a_0 = 4.76$, $b_0 = 3.70$	
Nucleation rate constant K_g	K^2	–			1.02×10^5	
Lateral surface free energy σ	erg cm^{-2}	–			8.0	
Fold surface free energy σ_e	erg cm^{-2}	–			40	
Melting point (equilibrium)	K	T_m (determined by $T_m - T_c$ extrapolation)			542.2	(44)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Deformation induced crystallization	—	Spinning effects	—	(7)
Glass transition temperature	K	Dependent on relative humidity (water plasticized)	320–330	(1)
		Oven dry	351	(7)
		50% RH	308	(7)
		100% RH	258	(7)
Melting point	K	General	537	—
		α I: monoclinic	543	
		α I: triclinic	534–574	
		α II: triclinic	542.5	
Sub-T_g transition temperatures	K	β (plasticized glass transition)		
		At 11 Hz	363	(61)
		—	357	(62)
		At 1 Hz	370	(63)
		γ (amide hydrogen bond motions with sorbed H_2O)		
		At 40–600 Hz	249	(64)
		—	245	(62)
		δ (methylene group motion)		
		At 40–600 Hz	156	(64)
		—	186	(62)
Heat capacity (of repeat units)	$kJ\,kg^{-1}\,K^{-1}$	DSC annealed nylon solid	1.4	(65)
Deflection temperature	K	Zytel ASTM D 648		(8)
		0.5 MPa	508	
		1.8 MPa	363	
Tensile modulus	MPa	Nylon 23°C	3,300	(10)
		Nylon 23°C moist ISO-1110	1,700	
		Nylon, 100°C	600	
Bulk modulus	MPa	Nylon dry crystalline rods	3,300	(10)
Shear modulus	MPa	23°C	1,300	(10)
		23°C (nucleated)	1,700	
		100°C	300	
		200°C	150	
Shear strength	MPa	Zytel Resins ASTM D 732, 23°C	66.8–72.4	(8)
		50% relative humidity, 23°C	63.4–68.9	
Storage modulus	MPa	0.1–110 Hz	5–100	(7)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Loss modulus	—	0.1–110 Hz, log tan δ	−1.3 to 0.9	(7)
Tensile strength	MPa	Zytel Resins ASTM D 638		(8)
		−40°C	113.8–128.9	
		23°C	82.7–90.3	
		77°C	58.6–62.1	
		121°C	42.7–47.6	
		50% relative humidity		
		−40°C	110.3–117.2	
		23°C	62.1–77.2	
		77°C	40.7–50.3	
		121°C	32.4–42.1	
Yield stress	MPa	Zytel Resins ASTM D 638		(8)
		−40°C	113.8–128.9	
		23°C	82.7–90.3	
		77°C	44.8–58.6	
		121°C	33.1–34.5	
		50% relative humidity		
		−40°C	110.3–117.2	
		23°C	58.6–62.1	
		77°C	39.3–40.7	
		121°C	27.6–32.4	
Yield strain $(L/L_0)_y$	%	Zytel Resins ASTM D 638		(8)
		−40°C	4–5	
		23°C	4–5	
		77°C	25–30	
		121°C	30–45	
		50% relative humidity		
		−40°C	5	
		23°C	25–30	
		77°C	30	
		121°C	30–40	
Maximum extensibility $(L/L_0)_r$	%	Zytel ASTM D 638		(8)
		−40°C	10–15	
		23°C	30–60	
		77°C	145–>300	
		121°C	200–>300	
		50% relative humidity		
		−40°C	15–35	
		23°C	200–>300	
		77°C	250–>300	
		121°C	>300	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Flexural modulus	MPa	Zytel ASTM D 790		(8)
		−40°C	3,241–3,516	
		23°C	2,827–2,964	
		77°C	689–724	
		121°C	538–552	
		50% relative humidity		
		−40°C	3,447	
		23°C	1,207–1,310	
		77°C	565–586	
		121°C	414	
Impact strength	$J\,m^{-1}$	Zytel ASTM D 256 Izod		(8)
		−40°C	32	
		23°C	53–64	
		50% relative humidity Izod		
		−40°C	27	
		23°C	112–133	
	$kJ\,m^{-2}$	Zytel ASTM D 1822 tensile impact, 23°C		
		Long specimen	504	
		50% RH long specimen	1,470	
		Short specimen	157	
		50% RH short specimen	231	
Compressive strength	MPa	20°C nylon molded 2.5% H_2O		
		1% strain	14	(10)
		2% strain	28	
		4% strain	56	
		6% strain	70	
Hardness	–	Zytel ASTM D676 Durometer	89	(8)
		50% Relative humidity	82	
Poisson ratio	–	General extruded rod	0.41	(8)
			0.38	(10)
		100°C	0.44	(10)
		Melt	0.5	(10)
Abrasion resistance	$g\,MHz^{-1}$	Zytel Taber abrasion CS-17 wheel, 1,000 g	4–7	(8)
Refractive index increment dn/dc	$ml\,g^{-1}$	(All data at 25°C)	(Source wavelength noted)	
		Formic acid 90% + 0.5 M sodium formate	0.137 (436 nm)	(66)
		Trifluroethanol	0.228 (436 nm)	(66)
(Trifluoroacetylated nylon 6,6)		Acetone	0.076 (436 nm)	(67)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Refractive index increment dn/dc	ml g^{-1}	(All data at 25°C)	(Source wavelength noted)	
		Formic acid		
		75%	0.144 (633 nm)	(39)
		80%	0.145 (633 nm)	(39)
		85%	0.141 (436 nm)	(68)
		90%	0.145 (633 nm)	(20, 39)
		90%	0.145 (546 nm)	(18)
		90%	0.145 (436 nm)	(68)
		95%	0.150 (633 nm)	(39)
		100%	0.157 (633 nm)	(39)
		100%	0.1525 (436 nm)	(69)
		Formic acid + KCl		(20)
		85% + 2.0 M KCl	0.124 (633 nm)	
		90% + 0.2 M KCl	0.143 (633 nm)	
		90% + 0.5 M KCl	0.140 (633 nm)	
		90% + 1.0 M KCl	0.136 (633 nm)	
		90% + 1.5 M KCl	0.131 (633 nm)	
		90% + 2.0 M KCl	0.126 (633 nm)	
		90% + 2.5 M KCl	0.122 (633 nm)	
		95% + 2.0 M KCl	0.129 (633 nm)	
		Formic acid + sodium formate		(39)
		75% + 0.5 M NaHCOO	0.138 (633 nm)	
		80% + 0.5 M NaHCOO	0.136 (633 nm)	
		90% + 0.02 M NaHCOO	0.147 (633 nm)	
		90% + 0.05 M NaHCOO	0.146 (633 nm)	
		90% + 0.10 M NaHCOO	0.142 (633 nm)	
		90% + 0.2 M NaHCOO	0.142 (633 nm)	
		90% + 0.5 M NaHCOO	0.136 (633 nm)	
		90% + 0.75 M NaHCOO	0.130 (633 nm)	
		90% + 1.0 M NaHCOO	0.124 (633 nm)	
		95% + 0.5 M NaHCOO	0.136 (633 nm)	
		100% + 0.5 M NaHCOO	0.136 (633 nm)	
		Tetrafluropropanol	0.190 (546 nm)	(24)
		Tetrafluropropanol + 0.1 N sodium trifluroacetate buffer	0.190 (436 nm)	(24)
Birefringence	–	$n_{\parallel}$	1.582	(51)
		$n_{\perp}$	1.519	(9)
Dielectric constant ε'	–	Zytel ASTM D 150		(8)
		1×10^2 Hz	4.0	
		1×10^3 Hz	3.9	
		1×10^6 Hz	3.6	
		1×10^2 Hz	8.0	
		50% relative humidity		
		1×10^3 Hz	7.0	
		1×10^6 Hz	4.6	
		–	(See also table below)	

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Dielectric constant ε'

Temp. (°C)	10^2 Hz	10^3 Hz	10^4 Hz	10^5 Hz	10^6 Hz	10^7 Hz	10^8 Hz	10^9 Hz
−30	120	105	105	130	165	160	100	49
0	110	120	135	160	200	200	160	81
30	85	125	180	215	250	255	220	135
60	810	590	460	390	370	360	320	240
90	2,000	1,450	1,300	1,450	1,600	1,300	810	440
20 (50% RH)	1,100	1,020	1,000	900	700	450	280	170

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric tan δ	—	Nylon (coupled with above table) values given as tan $\delta \times 10^4$	See table below	(10)

Dielectric tan δ

Temp. (°C)	10^2 Hz	10^3 Hz	10^4 Hz	10^5 Hz	10^6 Hz	10^7 Hz	10^8 Hz	10^9 Hz
−30	3.1	3.1	3.1	3.0	3.0	3.0	3.0	3.0
0	3.3	3.3	3.2	3.2	3.1	3.0	3.0	3.0
30	3.6	3.5	3.4	3.4	3.2	3.1	3.1	3.0
60	5.0	4.6	4.3	4.0	3.7	3.5	3.3	3.1
90	10	8.9	7.6	6.2	5.0	4.0	3.4	3.2
20 (50% RH)	7.5	5.9	4.8	4.1	3.7	3.4	3.3	3.2

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric strength	V cm^{-1}	VDE 0303, part 2, IEC-243, electrode K20/P50		(10)
		Dry	120×10^{-4}	
		Dry, 100°C	40×10^{-4}	
		Moist ISO-1110	80×10^{-4}	
Dissipation factor	—	Zytel ASTM D 150		(8)
		1×10^2 Hz	0.01	
		1×10^3 Hz	0.02	
		1×10^6 Hz	0.02	
		50% relative humidity		
		1×10^2 Hz	0.2	
		1×10^3 Hz	0.2	
		1×10^6 Hz	0.1	
Resistivity	ohm cm	Zytel ASTM D 257	1×10^{15}	(8)
		Zytel ASTM D 257, 50% RH	1×10^{13}	(8)
		Nylon, 20°C, 50% RH	3×10^{11}	(10)
		Nylon, 20°C, 100% RH	1×10^{9}	(10)
		Nylon, 60°C	6×10^{11}	(10)
		Nylon, 100°C	3×10^{9}	(10)
		Nylon, 100°C, 50% RH	4×10^{7}	(10)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Thermally stimulated current	–	Relaxation, humidity effects	–	(7)
Surface tension	$mN\ m^{-1}$	Nylon, $M_n = 17{,}000$, $M_w = 35{,}000$		
		20°C	46.5	(70)
		150°C	38.1	
		200°C	34.8	
		280°C	29.6	
		325°C	26.7	
		$-d\gamma/dT$	0.065	(41, 70)
		γ_{LV} at 20°C	46.4	(41)
		Zisman critical wetting surface tension, γ_c	42.5	(71)
Contact angle θ	Degrees	Water	72	(72)
Surface free energy	$mJ\ m^{-2}$	Dispersive, γ^D	40.8	(72)
		Polar, γ^P	6.2	(72)
		Lifschitz-van Der Waals, γ^{LW}	36.4	(73)
		Lewis Acid Base, γ^{AB}	1.3	(73)
		Electron acceptor parameter, γ^+	0.02	(73)
		Electron donor parameter, γ^-	21.6	(73)
Interfacial tension	$mN\ m^{-1}$	Polyethylene, γ_{12} at 20°C	14.9	(70)
	$mN\ m^{-1}\ K^{-1}$	$-d\gamma/dT$	0.018	
Adhesive bond strength	MPa	Nylon-aluminum tensile	68	(74)
		Nylon-steel tensile	70	
		Nylon-copper tensile	76	
Diffusion coefficient	$cm^2\ s^{-1}$	H_2O, 20°C	0.02×10^{-8}	(10)
		H_2O, 60°C	3.5×10^{-8}	(10)
		H_2O, 100°C	25×10^{-8}	(10)
		CO_2, 5°C, undrawn fiber	1.8×10^{-10}	(75)
		CO_2, 25°C, undrawn fiber	8.3×10^{-10}	(75)
		CO_2, 5°C, drawn fiber	1.8×10^{-10}	(75)
		CO_2, 25°C, drawn fiber	4.8×10^{-10}	(75)
Activation energy for diffusion	$kJ\ mol^{-1}$	H_2O	58	(10)
Permeability coefficient	cm^3 (STP) cm $s^{-1}\ cm^{-2}\ Pa^{-1}$	CO_2, 5°C, undrawn fiber	0.018×10^{-13}	(75)
		CO_2, 25°C, undrawn fiber	0.052×10^{-13}	(75)
		CO_2, 5°C, drawn fiber	0.023×10^{-13}	(75)
		CO_2, 25°C, undrawn fiber	0.071×10^{-13}	(75)
	cm^3 (NPT) m^{-2} $mil^{-1}\ atm^{-1}$	CO_2	140	(7)
		O_2	80	(7)
		N_2	5	(7)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Activation energy for permeation	—	CO_2	—	(75)
Solubility coefficient	cm^3 (STP) cm^{-3} Pa^{-1}	CO_2, 5°C, undrawn fiber CO_2, 25°C, undrawn fiber CO_2, 5°C, drawn fiber CO_2, 25°C, undrawn fiber	9.97×10^{-6} 6.32×10^{-6} 12.8×10^{-6} 14.8×10^{-6}	(75)
Thermal conductivity	$W\ m^{-1}\ K^{-1}$	Zytel resins	0.25	—
Melt viscosity	Pa s	Newtonian (shear stress <30 kPa) $[\eta] = 1.09\ dl\ g^{-1}$, $M_n = 14{,}000$ 270°C 280°C 290°C	40–1,000 110 70 50	(1)
Speed of sound	$m\ s^{-1}$	Longitudinal; density = $1.147\ g\ cm^{-3}$ Shear; density = $1.147\ g\ cm^{-3}$	2,710 1,120	(76)
Biodegradability, effective microorganisms	—	Wood Rotting Basidiomycetes	—	(7)
Heat of combustion	$kJ\ kg^{-1}$	—	−31.400	(51)
Decomposition products	K	H_2O, CO_2, cyclopentanone, hydrocarbons H_2O, CO_2, NH_3, cyclic monomomer, cyclopentanone, cyclopentylidinicyclopentanone, cyclopentylcyclopentanane, hexylamine, hexamethyleneimine, hexamethylene diamine	583–653 578	(77) (78)
Cross-linking, *G* factor	$mol\ J^{-1}$	Electron beam/γ irradiation	0.50	(79)
Gas evolution, *G* factor	$mol\ J^{-1}$	—	0.70	(79)
Water absorption	%	Zytel ASTM D 570 24 h immersion, 23°C Saturation, 23°C Annealed (Karl Fisher method)	 1.2 8.5 7	(8) (1)
Solvent absorption	%	Ethanol, 20°C, saturation Butanol, 20°C, saturation Glycol, 20°C, saturation Methanol, 20°C, saturation Propanol, 20°C, saturation	9–12 4–8 2–10 9–14 9–12	(10)
Oxygen index	%	Zytel ASTM D 2863	28–31	(8)

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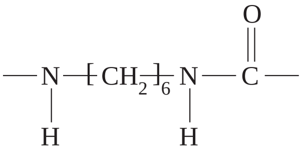
Nylon 6,6 copolymer

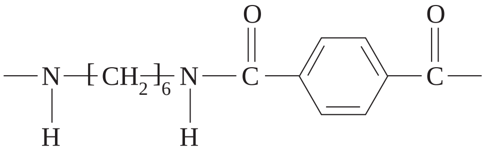
SHAW LING HSU

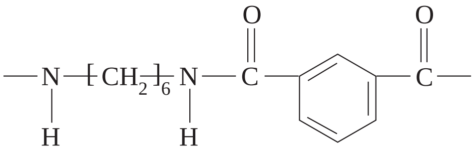
ACRONYM, ALTERNATIVE NAME, TRADE NAME PPA, polyphthalamide, Amodel (Amoco)

CLASS Aromatic polyamides; aromatic nylons

STRUCTURE As described in several articles and patents,[1,2] this type of aromatic nylon resin is a polyamide consisting of varying portions of aliphatic and aromatic units. Hexamethylene diamine is the main aliphatic component, which may be augmented by various amounts of adipic acid. The main aromatic component is terephthalic acid, which may be augmented by lesser amounts of isophthalic acid. Depending on relative composition, Amodel (nylon 6,6 copolymer) resins can be regarded as co- and terpolymers consisting of repeat units of nylon 66, nylon 6T, and nylon 6I—poly(hexamethylene isophthalamide). The major potential difference of other aromatic nylons, such as Ultramid T from BASF, is the presence of the 6I component.[1,2]

(Nylon 6) 

(Nylon 6T) 

(Nylon 6I) 

PROPERTIES OF SPECIAL INTEREST Because of the *p*-phenylene unit, extremely high melting temperature can be achieved. The degree of crystallinity, embrittlement, and transparency can all be controlled by adjusting the chemical composition (nylon 6I content).[3] Dimensional stability in the presence of moisture. Exceptional mechanical properties (modulus $> 2 \times 10^6$ psi, strength), creep resistance, and flexural strength.

MAJOR APPLICATIONS High temperature applications, industrial and chemical processing equipment, bearings and gears, aerospace components, appliance and plumbing parts, electrical/electronics applications such as connectors, under-hood automobile applications, packaging.

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
NMR*	ppm	Range for amide proton peaks	6–7	(4)
		Range for methylene proton peaks	1–4	
IR (characteristic absorption frequencies)	cm^{-1}	Overall, the infrared spectrum greatly resembles those found for other polyamides		(5–12)
		N–H stretching	3,305	–
		Amide I	1,627	–
		Amide II	1,545	–
		Methylene stretching vibrations	3,000	(7–9, 11–17)
		Methylene bending vibrations	1,400	(7–9, 11–17)
		Other specific spectroscopic features can be linked to the presence of the aromatic component		(2, 18)
		Vibrations assignable to para-disubsitituted aromatic units	862, 1,019, ~1,300,† 1,498	(9, 10, 19)
		Methylene/amide ratio is indicated by the ratio of the integrated band intensity at 3,000 cm^{-1} to that at 3,305 cm^{-1}		(9, 20)
Melting temperature‡	K	Range (depending on composition)	543–593	(21)
		For Amoco products	585	
Glass transition temperature	K	Depending on composition	400	(22)
			362–408	(22)
			399	(3)
Density	$g\,cm^{-3}$	–	1.27	(22)
Moisture uptake	%	23°C, saturation 23°C, 50% RH 23°C, 100% RH	62.55.9	(3)
Melt viscosity	poise	325°C	3,000	(22)
Degradation of aromatic polyamides by radiation	Plasma treatment can modify aromatic nylons reducing the relative concentration of amide units relative to that in untreated nylon 6,6 copolymer. These aromatic nylons can also be hydrolyzed in acid solutions.			(23)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	40°C	0.24	(22)
Modulus	psi	Strength	$>2 \times 10^6$	–
Tensile strength	MPa	–	103–117	(22)
Yield stress	MPa	–	103–117	(22)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Yield strain	%	—	3	(22)
Flexural modulus	MPa	—	3,500–3,800	(22)
Flexural strength	MPa	—	310	—
Degree of crystallinity	%	—	22–28	(22)
Deflection temperature	K	—	363–403	(22)
Solvents	Hexafluoroisopropanol (HFIP), hot sulfuric acid, hot phenol			(22)

[*]Both assignments fall into the range of peak positions listed for these groups in standard NMR tables.
[†]Broad features.
[‡]DSC melting curves associated with aromatic nylons have been reported for various compositions of the two components.

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Nylon 6,10

MELVIN I. KOHAN

ACRONYMS, TRADE NAMES PA 610, PA-610, Nylon-610, Amilan (Toray), Technyl D (Rhone Poulenc), Ultramid S (BASF)

CHEMICAL NAMES Poly(hexamethylene sebacamide), poly(hexamethylene decanoamide), poly(iminohexamethylene-iminosebacoyl), poly[imino-1,6-hexanediylimino(1,10-dioxo-1,10-decanediyl)] (CAS Registry No. 9008-66-6)

CLASS Aliphatic polyamides

STRUCTURE $-[NH(CH_2)_6NHCO(CH_2)_8CO]-$
This most often is not a pure homopolymer because the sebacic acid made from castor oil that is used in the commercial synthesis is not the 100% pure dibasic acid.

MAJOR APPLICATIONS Monofilament, hardware, industrial parts, and precision instruments.

PROPERTIES OF SPECIAL INTEREST Relatively low melting point; resistance to solvents, particularly hydrocarbons, and resistance to aqueous zinc chloride; low water absorption; stiffness; abrasion resistance; dimensional stability.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight	$g\,mol^{-1}$	Per amide group	141.21	—
		Per repeat unit	282.42	
Typical moleculare weight range	$g\,mol^{-1}$	—	11,000–20,000	(1)
Typical polydispersity index, M_m/M_n (M_w/M_n)	—	—	2.0	—
Density	$g\,cm^{-3}$	Crystalline, α, triclinic	1.156	(2)
		Crystalline	1.152	(4)
		Typical injection molded	1.07-1.09	—
		Melt 270°C, 1 bar	0.913	(5)
		Melt 230–290°C	0.91–0.94	(1)
		Amorphous	1.05	(3)
		Amorphous	1.041	(4)
IR (characteristic absorption frequencies)	cm^{-1}	N-vic. CH_2 bend (α)	1,474	(6)
		CH_2 bend	1,466	
		CH_2 bend	1,437	
		CO-vic. CH_2 bend (α)	1,419	
		Amide III (?)	1,284	
		(α)	1,191	
		(γ, amorphous)	1,180	
		(amorphous)	1,133	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
IR (characteristic absorption frequencies)		C–CO stretch (α or γ)	938	
		CH_2 wag	730	
		Amide V (α)	689	
		Amide VI (α)	583	
NMR	–	–	–	(7)
Coefficient of linear thermal expansion	K^{-1}	–	9.0×10^{-5}	–
Compressibility of the melt	Pa^{-1} (bar^{-1})	–	~ 5 ($\sim 5 \times 10^{-5}$)	(1)
PVT curves				(8)
Reduction temperature T^*	K	–	8,240	
Reduction pressure P^*	MPa	–	661	
Reduction volume V^*	$cm^3\ g^{-1}$	–	0.845	
Solvents	–	25°C	Concentrated sulfuric acid, *m*-cresol	–
		Redissolution, 156°C	Ethylene glycol	(9)
		Redissolution, 139°C	Propylene glycol	(9)
Mark–Houwink parameters: K and a	$K = cm^3\ g^{-1}$ $a =$ None	*m*-Cresol, 25°C, for M_n = 8,000–24,000	$K = 13{,}500$ $a = 0.96$	(10)
Polymers with which compatible		–	–	(22)
Unit cell dimensions	Å	α-Triclinic	$a = 4.95$, $b = 5.4$, $c = 22.4$	(2)
		β-Triclinic	$a = 4.9$, $b = 8.0$, $c = 22.4$	
Unit cell angles	Degrees	α-Triclinic	$\alpha = 49$, $\beta = 76.5$, $\gamma = 63.5$	(2)
		α-Triclinic	$\alpha = 90$, $\beta = 77$, $\gamma = 67.5$	
Units in cell	–	α-Triclinic	1	(2)
		β-Triclinic	2	
Degree of crystallinity	%	Range, injection molded	25–45	(11)
Heat of fusion (per repeat unit)	$kJ\ mol^{-1}$ ($kJ\ kg^{-1}$)	Crystalline, from ΔH_m, DTA	56.8 (201)	(12)
		Crystalline, from ΔH_m, DTA	54.6 (193)	(13)
		Crystalline, from sp. ht.	53.2 (188)	(14)
Entropy of fusion (per repeat unit)	$J\ K^{-1}\ mol^{-1}$	Crystalline	110–114	(18)
Glass transition temperature	K	Dry, mech. loss peak	340	(15)
		Dry, flex. mod. vs. temp.	343	(15)
		Dry, DTA	315	(16)
		50% RH, mech. loss peak	313	(15)
		100% RH, mech. loss peak	283	(15)

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Melting point	K	X-ray	500		(17)
		DTA			(17)
		Start	494		
		Peak	497		
		End	499		
		Equilibrium	≥510		(29)
			Range	Average	
		Fisher-Johns	489–496	492	(17)
		Capillary	485–494	490	(17)
		Köfler hot stage	485–503	493	(17)
Heat capacity (per repeat unit)	$J\ K^{-1}\ mol^{-1}$	—	502		(19)
Deflection temperature	K	ASTM D 648 = DIN 53461 = ISO 75			(20, 21)
		Dry			
		455 kPa	430–448		
		1,820 kPa	339		
		50% RH			
		455 kPa	433		
		1,820 kPa	333		
Tensile properties, ASTM D 638 = DIN 53455 = ISO 527					
Tensile modulus	MPa	23°C			(20, 21)
		Dry	2,400		
		50% RH	1,500		
Tensile strength	MPa	−40°C			(20, 21)
		Dry	83		
		50% RH	83		
		23°C			
		Dry	59		
		50% RH	49		
		77°C			
		Dry	37		
		50% RH	37		
Yield stress	MPa	−40°C			(20, 21)
		Dry	83		
		50% RH	83		
		23°C			
		Dry	60		
		50% RH	50		
		77°C			
		Dry	37		
		50% RH	37		

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Yield strain $(L/L_0)_y$	%	−40°C		(20, 21)
		Dry	10	
		50% RH	13	
		23°C		
		Dry	10	
		50% RH	30	
		77°C		
		Dry	30	
		50% RH	–	
Maximum extensibility $(L/L_0)_r$	%	−40°C		(20, 21)
		Dry	20	
		50% RH	30	
		23°C		
		Dry	70–100	
		50% RH	≥150	
		77°C		
		Dry	300	
		50% RH	–	
Flexural modulus	MPa	ASTM D 790 = DIN 53457 = ISO 178		(20, 21)
		−40°C		
		Dry	2,240	
		50% RH	2,520	
		23°C		
		Dry	2,000	
		50% RH	1,100	
		100% RH	690	
		77°C, dry	480	
Bulk modulus	MPa	25°C	2,300	(24)
Shear strength	MPa	ASTM D 732, 23°C, dry	58	(21)
Impact strength (cf. ASTM D 256, DIN 53453, ISO 179)	$J\,m^{-1}$	Notched Izod, 23°C		(20, 21)
		Dry	50	
		50% RH	200	
	$kJ\,m^{-2}$	Charpy, 20°C		(21)
		Dry	4–10	
		65% RH, 4 months	13–15	
Hardness		ASTM D 785; 23°C		
	M scale	Dry	75	(20, 21)
	M scale	50% RH	60	(20, 21)
	R scale	Dry	110–111	(21)
Poisson ratio	–	20°C ,moldings	0.3–0.4	(5)
		100°C	0.47	
		Melt	0.50	

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Nylon 6,10

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Abrasion resistance, Taber	$mg\,kHz^{-1}$	C17 wheel, 1 kg	5–6	(21)
Index of refraction	—	25°C, molded, undrawn	1.532	(11)
		Isotropic	1.52	
		Parallel	1.57	
		Perpendicular	1.52	
Dielectric constant	—	ASTM D 150, IEC 250		
		Dry		(21)
		50–100 Hz	3.9	
		1 kHz	3.6	
		1 MHz	3.3	
		−30, 0°C; 100 Hz–1 GHz	3.0	(5)*
		30°C		(5)
		100 Hz–1 kHz	3.2	
		1 MHz–1 GHz	3.0	
		60°C		(5)
		100 Hz	4.6	
		1 kHz	4.2	
		1 MHz	3.4	
		1 GHz	3.0	
		90°C		(5)
		100 Hz	13	
		1 kHz	10.5	
		1 MHz	5.2	
		1 GHz	3.1	
		20°C, 65% RH		(5)
		100 Hz	6.5	
		1 kHz	5.4	
		1 MHz	3.5	
		1 GHz	3.0	
Dissipation factor, dielectric loss	—	ASTM D 150, IEC 250		
		Dry		(21)
		50–100 Hz	0.04	
		1 kHz–1 MHz	0.03	
		−30°C		(5)*
		100 Hz	0.012	
		1 kHz	0.011	
		1 MHz	0.015	
		1 GHz	0.006	
		0°C		(5)
		100 Hz–1 kHz	0.013	
		1 MHz	0.017	
		1 GHz	0.010	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dissipation factor, dielectric loss	–	30°C		(5)
		100 Hz	0.010	
		1 kHz	0.015	
		1 MHz	0.021	
		1 GHz	0.013	
		60°C		(5)
		100 Hz	0.090	
		1 kHz	0.065	
		1 MHz	0.054	
		1 GHz	0.025	
		90°C		(5)
		100 Hz	0.250	
		1 kHz	0.170	
		1 MHz	0.190	
		1 GHz	0.035	
		20°C; 65% RH		(5)
		100 Hz	0.200	
		1 kHz	0.150	
		1 MHz	0.080	
		1 GHz	0.020	
Volume resistivity	ohm cm	ASTM D 257, IEC 93		
		Dry		(5, 21)
		20°C	10^{15}	
		60°C	5×10^{11}	
		100°C	5×10^{8}	
		20°C		(5)
		50% RH	2×10^{12}	
		100% RH	3×10^{10}	
Surface tension	$mN\,m^{-1}$	Melt, 265°C	37	(23)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	–	0.23	(21)
		Amorphous, moist, 30°C	0.35	(24, 25)
		Dependence on pressure, λ(25 kbar)/λ (atm. pressure); 25°C	1.90	(24, 25)
Melt viscosity	Pa s	Commercial injection molding grade resin, 280°C		(26)
		$10\ s^{-1}$	37	
		$10^2\ s^{-1}$	34	
		$10^3\ s^{-1}$	27	
		$10^4\ s^{-1}$	14	
Activation energy of viscous flow	$kJ\,mol^{-1}$	–	60	(27)
Coefficient of friction	–	Thrust washer, 275 kPa, $0.25\,m\,s^{-1}$		(28)
		Static	0.23	
		Dynamic	0.31	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Limiting PV against steel	kPa m s^{-1}	0.5 m s^{-1}	70	(28)
Water absorption	%	50% RH	1.4–1.5	—
		100% RH	3.3 ± 0.3	(5)
Solvent absorption	%	Ethanol, 20°C, saturation	8–13	(5)
		Butanol, 20°C, saturation	8–12	
		Glycol, 20°C, saturation	2–4	
		Methanol, 20°C, saturation	16	
		Propanol, 20°C, saturation	10	
Oxygen index	%	ASTM D 2863, dry	24	(5)

*Moisture content unspecified, but data indicate dry specimens.

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Nylon 6,12

GUS G. PETERSON AND W. BROOKE ZHAO

ALTERNATIVE NAMES Poly[imino-1,6-hexanediylimino(1,12-dioxo-1,12-dedecanediyl)]

CLASS Aliphatic polyamides

STRUCTURE $\left[(CH_2)_6 - NH - \overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_{10} - \overset{\overset{\displaystyle O}{\|}}{C} - NH \right]$

MAJOR APPLICATIONS Engineering resin

PROPERTIES OF SPECIAL INTEREST Low water absorption compared to Nylon 6,6

PREPARATIVE TECHNIQUES Polycondensation of hexamethylenediamine and dodecanedioic acid

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	Size-exclusion chromatography	25,700 ± 700	(1)
IR (characteristic absorption frequencies)	cm^{-1}	N−H stretching C=O stretching (amide I band)	3,050 1,650–1,634	(2)
NMR (15N)	ppm	32°C 36°C 42°C 49°C 56°C	119.8 119.8 119.8 119.7 119.6	(3)
Thermal expansion coefficient	K^{-1}	Linear	9×10^{-5}	(2)
Density	$g\,cm^{-3}$	–	1.06	(4)
Common solvents	Phenols, formic acid, chloral hydrate, fluorinated alcohols, mineral acids			(2)
Contact angle	Degrees	*c*-Hex *i*-Oct	113.9 ± 1.0 109.0 ± 0.8	(5)
Equilibrium heats of fusion ΔH_f^0	$kJ\,mol^{-1}$	–	80.1	(6)
Glass transition temperature T_g	K	–	319	(6)
Melting temperature T_m	K	–	520–480	(6)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat capacity	$kJ\ K^{-1}\ mol^{-1}$	230°C	0.382	(7)
		300°C	0.494	
		400°C	0.771	
		600°C	0.981	
Deflection temperature	K	0.455 MPa	453	(2)
		1.82 MPa	363	
Brittleness temperature	K	—	164	(2)
Specific heat	$kJ\ K^{-1}\ mol^{-1}$	—	0.525	(2)
Tensile strength	MPa	—	60.7	(2)
Yield stress	MPa	—	51.0	(2)
Elongation at break	%	—	$\geq$300	(2)
Elongation at yield	%	—	25	(2)
Shear strength	MPa	Dry	55.8	(2)
Flexural modulus	MPa	—	1,241	(2)
Izod impact strength	$J\ m^{-1}$	—	75	(2)
Dielectric constant ε'	—	—	5.3×10^3	(2)
Volume resistivity	ohm cm	—	10^{13}	(4)
Dissipation factor	—	1,000 Hz	0.15	(2)
Dispersion force component of surface free energy γ_S^d	$mJ\ m^{-2}$	—	62 ± 9	(5)
Nondispersive interaction free energy between solid and water I_{SM}^n	$mJ\ m^{-2}$	—	30.7 ± 0.4	(5)
Polar surface free energy γ_S^p	$mJ\ m^{-2}$	—	4.7	(5)
Surface free energy γ_S	$mJ\ m^{-2}$	—	67	(5)
Thermal conductivity	$W\ m^{-1}\ K^{-1}$	—	0.22	(2)
Intrinsic viscosity	$dL\ g^{-1}$	—	1.45	(8)
Water absorption	%	At saturation	3.0	(2)
Flammability, oxygen index	—	—	28	(2)

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Nylon 11

GEORGE APGAR

ACRONYMS, TRADE NAME Polyamide 11, PA-11, Rilsan® B (Elf Atochem)

CLASS Aliphatic polyamides

STRUCTURE $[-C{=}O-(CH_2)_{10}-NH-]$

MAJOR APPLICATIONS Tubing, hoses, and pipes for automotive, trucking, industrial, and petroleum production applications. Examples are heavy truck airbrake tubing, automotive fuel lines, and submarine flexible pipes for offshore oil production. Thermoplastic powder coatings for industrial, transportation, and retail items are prepared in a Nylon 11 base. Nylon 11 has be used in a variety of food-contact applications, including sausage casing, beverage tubing, and reusable kitchen devices.

PROPERTIES OF SPECIAL INTEREST Nylon 11 has low moisture absorption relative to other nylons. Specific gravity is also low. Chemical resistance to hydrolytic reagents is unusually good for a polyamide. Modulus is low, which provides superior impact properties at both ambient and subambient temperatures.

PREPARATIVE TECHNIQUES Nylon 11 is prepared by a condensation polymerization reaction. The commercial monomer is 11, aminoundecanoicacid. This aminoacid is unique among the nylon monomers because it is made from castor oil, a renewable, agricultural raw material. The 18-carbon ricinoleicacid is thermally cracked to 7-carbon and 11-carbon fractions. The 11-carbon portion has an omega unsaturation, which is hydrobrominated then aminated to the aminoacid monomer.[1]

PROPERTY*	UNITS	CONDITIONS	VALUE	REFERENCE
Common form	—	—	α, triclinic	(2)
Unit cell dimensions	Å	*a* axis	4.9	(2)
		b axis	5.4	
		c axis	14.9	
Angles	Degrees	Alpha	40	(2)
		Beta	77	
		Gamma	63	
Density, crystalline	$g\,cm^{-3}$	—	1.15	(2)
Density, amorphous	$g\,cm^{-3}$	25% crystallinity is typical after melt processing	1.01	(2)
Water absorption	wt%	Equilibration at		(2)
		23°C, 65% RH	1.1	
		23°C, 100% RH	1.9	
		100°C, 65% RH	3.0	

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Nylon 11

PROPERTY*	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of fusion	$J g^{-1}$	24% crystallinity	39	(2)
Specific heat	$J g^{-1} K^{-1}$	23°C 250°C	1.752.6	(2)
Glass transition temperature	K	–	315	(2)
Thermal conductivity	$W m^{-1} K^{-1}$	–	0.19	(3)
Mark–Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None	For PA-11; mol. wt. = 1.8–9×10^4 at 30°C in *m*-Cresol	$K = 91$ $a = 0.69$	(4)
Melt viscosity	Poise	For commercial grades of PA-11; 240°C; $500 s^{-1}$ shear rate	1,000–7,000	(5)
Dielectric constant	–	Dry, 10^6 Hz	3.1	(6)
Dissipation factor	–	Dry, 10^6 Hz	0.04	(6)
Specific gravity	–	23°C		(2)
		Unmodified	1.03	
		Plasticized	1.05	
		43% glass	1.36	
Melting point	K	Unmodified	461	(2)
		Plasticized	457	
		43% glass	461	
Yield stress	MPa	23°C		(2)
		Unmodified	36	
		Plasticized	21	
Yield elongation	%	23°C		(2)
		Unmodified	22	
		Plasticized	26	
Break stress	MPa	−40°C		(2)
		Unmodified	72	
		Plasticized	76	
		23°C		
		Unmodified	68	
		Plasticized	62	
		43% glass	145	
		80°C		
		Unmodified	66	
		Plasticized	54	

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PROPERTY*	UNITS	CONDITIONS	VALUE	REFERENCE
Break elongation	%	−40°C		(2)
		Unmodified	160	
		Plasticized	220	
		23°C		
		Unmodified	360	
		Plasticized	380	
		43% glass	8	
		80°C		
		Unmodified	420	
		Plasticized	420	
Flexural modulus	MPa	−40°C		(2)
		Unmodified	1,586	
		Plasticized	2,275	
		23°C		
		Unmodified	1,269	
		Plasticized	310	
		43% glass	8,480	
		80°C		
		Unmodified	255	
		Plasticized	159	
Izod impact strength	$J\,m^{-1}$	-40°C		(2)
		Unmodified	27	
		Plasticized	21	
		23°C		
		Unmodified	99	
		Plasticized	No break	
		43% glass	247	
		80°C		
		Unmodified	NB	
		Plasticized	NB	
Deflection temperature	K	Unmodified	320	(2)
		Plasticized	313	
		43% glass	452	
Rockwell hardness	–	23°C		(2)
		Unmodified	R108	
		Plasticized	R75	
		43% glass	R111	
Hardness	Shore D values	23°C		(2)
		Unmodified	72	
		Plasticized	63	

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PROPERTY*	UNITS	CONDITIONS	VALUE	REFERENCE
Coefficient of linear thermal expansion	K^{-1} ($\times 10^{-5}$)	−30 to 50°C		(2)
		Unmodified	8.5	
		Plasticized	11	
		43% glass	7	
		50–120°C		
		Unmodified	15	
		Plasticized	21	
		43% glass	13	
Volume resistivity	ohm cm	500 VDC; 20°C		(2)
		Unmodified	1,014	
		Plasticized	1,011	
		43% glass	1,014	
Surface resistivity	ohm	20°C		(2)
		Unmodified	1,014	
		Plasticized	1,011	
		43% glass	1,014	
Dielectric strength	kV mm^{-1}	20°C		(2)
		Unmodified	30	
		Plasticized	24	
		43% glass	45	

*All properties measured in a dry, as-molded state.

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Nylon 12

H. ULF W. ROHDE-LIEBENAU

ACRONYMS, TRADE NAMES PA 12, polyamide 12, polydodecanolactam, polylaurolactam; Daiamid® (Daicel Chemical Industries); Grilamid® (EMS Chemie); Rilsan® A (Elf Atochem); UBE Nylon 12® (UBE Industries); Vestamid® (Creanova)

CLASS Aliphatic polyamides

STRUCTURE $-[NH_2-(CH_2)_{11}-CO]_p-$

PROPERTIES OF SPECIAL INTEREST Hydrolytic polycondensation at 260–300°C. Very low monomer content in melt-equilibrium. Activated anionic polymerization = monomer casting (small market volume). PA 12 crystallizes in pseudo-hexagonal modification. Combination of typical nylon and polyolefin properties. Low moisture absorption and density, chemical resistance similar to other nylons, not sensitive to stress cracking. Good to excellent impact strength, in dry state or at low temperatures. Engineering plastic, can be modified by glass or carbon fiber reinforcement, plasticizer, or other additives. PA 12 copolymers with PTHF: polyether block amides (PEBA)—see below.[1]

MAJOR APPLICATIONS Multiplicity of applications in technical engineering, especially in automotive and electrical industries. Antistatic parts. Precision molding. Sports and leisure goods. Coatings by extrusion, fluidized bed, or electrostatic process.

GENERAL INFORMATION Most properties were determined by relevant ISO and IEC standards in accordance with CAMPUS®. Three grades from the vast range of grades were selected: (1) unmodified extrusion, (2) with ~13% plasticizer, and (3) 30% glass fiber modified grade. (See ISO 1874-2 for a list of relevant standards.)

PROPERTIES	UNIT	CONDITIONS	VALUE			REFERENCE
			Unmodified	Plasticized	30% glass fiber	
Density	$g\ cm^{-3}$	Standard: ISO 1183				
		At 23°C	1.01–1.02	1.03	1.24	(2–4)
		Annealed at 160°C	1.028	Monomer casting	—	(2–4)
		At 260°C (melt)	~0.86	~0.88	~1.04	(5)
Moisture absorption	%	Standard: DIN 53495				(2–4)
		23°C, 50% RH	0.8	0.7	0.4–0.5	
		23°C, immersed	1.5	1.4	1.1	
Melting range	K	Polarization microscopy	448–453			(2–4)
Heat deflection temperature	K	Standard: ISO 75; load = 0.45 MPa	388	363	448	(2–4)

PROPERTIES	UNIT	CONDITIONS	VALUE			REFERENCE
			Unmodified	Plasticized	30% glass fiber	
Vicat softening point	K	Standard: ISO 306; load = 10 N	443	433	448	(2–4)
Glass transition temperature	K	Standard: ISO 537; tan δ by torsional pendulum				(2–4)
		Dry as molded	328			
		50% RH (=0.7% H_2O)	318			
Thermal expansion coefficient	K^{-1} ($\times 10^{-4}$)	Standard: DIN 53752; for 23–80°C				(2–4)
		In flow direction	1.5	1.8	0.6	
		Perpendicular direction	1.1	1.5	–	
Specific heat	$J\,g^{-1}\,K^{-1}$	Solid (23–60°C)	2.0	–	1.6	(3)
		Melt (250°C)	2.9	3.0	2.5	
Heat of fusion	$J\,g^{-1}$	–	65–75[a]	–	35–40[b]	(3)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	20–100°C	0.24	0.23	0.29	(3)
Melt volume index	ml $(10\,\text{min})^{-1}$	275°C $(5\text{ kg load})^{-1}$	~36	~60	~30	(5)
Maximum use temperature	K	Standard: UL 746B	358	353	378	(UL 746)
Flammability	Most PA 12 grades are slow burning (HB acc. UL 94), but there are self-extinguishing grades					(UL 94)
Oxygen index	%	Unmodified PA 12	21–22			(5)
Tensile modulus	MPa	Standard: ISO 527; equilibrated to 50% RH	1,450	400	6,500	(2–4)
Yield stress	MPa	Standard: ISO 527; equilibrated to 50% RH	46	26	130	(2–4)
Strain at yield	%	Standard: ISO 527; equilibrated to 50% RH	5	30	5	(2–4)
Strain at break	%	Standard: ISO 527; equilibrated to 50% RH	>200	>200	5–6	(2–4)
Notched impact strength (Izod)	$kJ\,m^{-2}$	Standard: ISO 180/1A; equilibrated to 50% RH				(2–4)
		At 23°C	20	No break	24	
		At –30°C	7	6	20	

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PROPERTIES	UNIT	CONDITIONS	VALUE: Unmodified	VALUE: Plasticized	VALUE: 30% glass fiber	REFERENCE
Notched impact strength (Charpy)	kJ m^{-2}	Standard: ISO 179; equilibrated to 50% RH	A[c]	B[d]		(2–4)
		At 23°C	6	20		
		At −30°C	5	7		
Dielectric constant ε'	–	Standard: IEC 250; 1 MHz; equilibrated to 50% RH	3.0	3.8	3.4	(4)
Dielectric loss ε''	–	Standard: IEC 250; 1 MHz; equilibrated to 50% RH	280×10^{-4}	$1{,}500 \times 10^{-4}$	230×10^{-4}	(4)
Dielectric strength	kV mm^{-1}	Standard: IEC 243; equilibrated to 50% RH	26	31	44	(4)
Surface resistivity R_{OA}	ohm	Standard: IEC 93; equilibrated to 50% RH	10^{13}	10^{12}	10^{13}	(4)
Volume resistivity	ohm cm	Standard: IEC 93; equilibrated to 50% RH	10^{15}	10^{12}	10^{15}	(4)
Comp. tracking index	–	Standard: IEC 112; equilibrated to 50% RH	600	600	>600	(4)
Molecular mass	g mol^{-1}	–	$M_n = 1.4\text{–}3.0\ (\times 10^4)$ $M_w = 3.5\text{–}10.5\ (\times 10^4)$			(6–8)
Typical polydispersity index (M_w/M_n)	–	–	2.5–3.5			(6–8)
Mark-Houwink parameters: K and a	K = ml g^{-1} a = None	–	$K = 524 \times 10^{-4}$ $a = 0.73$			(6–8)
Degree of crystallinity	%	Cooled After annealing at 150°C	~0.3 0.35–0.40			–
Unit cell dimensions	Pseudohexagonal gamma-modification with unit cell dimensions					(2, 3)
Lattice	–	–	Pseudohexagonal			(2, 3)
Unit cell content (number of repeat units)	–	–	4			(9)

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PROPERTIES	UNIT	CONDITIONS	VALUE			REFERENCE
			Unmodified	Plasticized	30% glass fiber	
Cell dimensions	nm	—	$a = 0.479$, $b = 3.19$, $c = 0.958$			(9)
Cell angle	Degrees	—	$\beta = 120$			(9)
Density (crystalline)	g cm^{-3}	Also unstable monoclinic α modification	1.106[e]			(10)
Index of refraction n_D^{25}	—	Only film and thin quenched parts are transparent	1.52–1.53			(5)

[a] Range = 160–195°C. [b] Range = 155–185°C.
[c] A = low molecular weight/injection molding. [d] B = high molecular weight/extrusion.
[e] Some sources give the crystalline density as 1.03 to 1.05 g cm^{-3}, which is too low. If one extrapolates data from reference (11) or if a parallel for nylon 12 is drawn to the line of density vs. crystallinity for nylon 11 from reference (12), then one can derive the approximate crystalline density of 1.10 g cm^{-3}.

Polyether block amides (PEBA) are internally plasticized by copolycondensation of PA 12 and PTHF block segments. The grades are differentiated by Shore hardness D as a measure of flexibility. In addition to typical PA 12 application ranges, PEBA are used for seals, gaskets and in medical devices. (Trade name of these grades of Elf Atochem is Pebax®)

PROPERTY	UNITS	[STANDARD]/ CONDITIONS	SHORE D HARDNESS*				PA 12	REFERENCE
			35	47	55	62		
Density	g cm^{-3}	[ISO 1183]	1.01	1.02	1.03	1.03	1.01–1.02	(1–3)
Tensile modulus	MPa	[ISO 527]	—	120	230	370	1,450	(1–3)
Yield stress	MPa	[ISO 527]	—	—	—	24	47	(1–3)
Tensile strength	MPa	[ISO 527]	17	23	32	—	—	(1–3)
Strain at break	%	[ISO 527]	>200	>200	>200	>200	>200	(1–3)
Notched impact strength (Izod)	kJ m^{-2}	[ISO 180/1A]						(1–3)
		At 23°C	No break	No break	No break	No break	20	
		At −30°C	No break	No break	22	8	7	
Heat deflection temperature	K	[ISO 75]; load 0.45 MPa	328	338	363	373	393	(1–3)
Vicat softening point	K	[ISO 306]; load 10 N	398	413	433	438	443	(1–3)

*Standard: ISO 868.

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Suppliers

EMS Chemie AG, Domat, Switzerland
Elf Atochem S.A., Paris, France
UBE Industries, Tokyo, Japan
Creanova GmbH., Division of Degussa-Hüls AG., Marl, Germany

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Nylon MXD6

AKIRA MIYAMOTO

TRADE NAME Reny (Mitsubishi Gas Chemical Co.)

CLASS Aliphatic polyamides

STRUCTURE $H{-}[NHCH_2{-}m{-}C_6H_4CH_2NHCO(CH_2)_4CO]_n{-}OH$

MAJOR APPLICATIONS Blow molded bottles. Extruded film and sheets for food packaging, including blend, multilayer, and laminate with nylon 6, PET, and polyolefins. Monofilament for bristle and filter cloth. Glass fiber reinforced injection molding materials used to make parts for the automotive, machine, electrical/electronic, civil engineering, sports, and other industries as a metal substitute.

PROPERTIES OF SPECIAL INTEREST Relatively low cost. High mechanical strength, modulus, and heat resistance. Very low oxygen permeability in humid atmosphere.

TYPE OF POLYMERIZATION Polycondensation in melt or solid phase

TYPICAL COMONOMERS *p*-Xylylenediamine

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	246.31	(1)
Typical molecular weight range	$g\,mol^{-1}$	End group titration	$(1.6–4.0) \times 10^4$	(6)
IR	cm^{-1}	Ref. KBr tablet	1,650; 1,550; 1,440; 1,030; 790; 700	(6)
UV	nm	Ref. 96% H_2SO_4	260	(7)
^{1}H-NMR	ppm	Formic acid solution	1.8, 2.5, 4.5, 7.3	(6)
^{13}C-NMR	ppm	Formic acid solution	25.7, 36.3, 44.7, 127.7, 130.0, 138.7, 177.7	(6)
Thermal expansion coefficient	K^{-1}	ASTM D696	5.1×10^{-5}	(1)
Density (amorphous)	$g\,cm^{-3}$	296 K	1.19	(6)
Solvents	—	Room temp.	Sulfuric acid, formic acid, trifluoroacetic acid, *m*-cresol, *o*-cresol, phenol/ethanol (4:1 by vol), hexafluoroisopropanol	(6)
		433 K	Benzyl alcohol, ethylene glycol	
		473 K	Diethylene glycol, triethylene glycol	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Nonsolvents	—	Room temp.	Water, *n*-butanol, *n*-heptane	
Crystalline state	—	Lattice Space group Chain conformation	Triclinic C_i^1-P1 Planes incline to the *c* axis by a few degrees from planar zigzag	(5)
Unit cell dimensions	Å	—	$a = 12.01$, $b = 4.83$, $c = 29.8$	(5)
Unit cell angles	Degrees	—	$\alpha = 75.0$, $\beta = 26.0$, $\gamma = 65.0$	(5)
Unit cell contents	—	—	2	(5)
Degree of crystallinity	%	Solid phase polymerized, DSC	35	(6)
Heat of fusion	$kJ\,mol^{-1}$	DSC	37	(6)
Density (crystalline)	$g\,cm^{-3}$	—	1.25	(5)
Glass transition temperature	K	DSC	358	(6)
Melting point	K	DSC	510	(6)
Heat capacity	$J\,K^{-1}\,g^{-1}$	DSC 313 K 533 K	 1.31 2.51	(6)
Deflection temperature	K	ASTM D648, 1.8 MPa	369	(1)
Tensile modulus	MPa	ASTM D638 dry	4,700	(1)
Tensile strength	MPa	ASTM D638 dry	99	(1)
Maximum extensibility (L/L_0)	%	ASTM D638 dry	2.3	(1)
Flexural modulus	MPa	ASTM D790 dry	4,400	(1)
Flexural strength	MPa	ASTM D790 dry	160	(1)
Impact strength	$J\,m^{-1}$	ASTM D256 dry, notched	20	(1)
Hardness	Rockwell M	ASTM D785 dry	108	(1)
Abrasion resistance	$g\,kcycles^{-1}$	ASTM D1044	19×10^{-3}	(2)

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Nylon MXD6

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Index of refraction n	–	ASTM D542, amorphous	1.582	(6)
Dielectric constant ε'	–	ASTM D150, 110 and 10^3 MHz	3.9	(2)
Dielectric loss index ε''	–	ASTM D150, 110 and 10^3 MHz	0.039	(2)
Resistivity	ohm cm	ASTM D257	1.2×10^{16}	(2)
Permeability coefficient	m^3 (STP) m s^{-1} m^{-2} Pa^{-1}	O_2, 296 K, 60% RH	5.7×10^{-21}	(6)
Thermal conductivity	W m^{-1} K^{-1}	–	0.38	(2)
Melt viscosity	Pa s	543 K, shear stress 24.5 kPa		(1)
		$M_n = 16,000$	140	
		$M_n = 19,000$	280	
		$M_n = 25,000$	730	
		$M_n = 39,000$	2,400	
Melt index	g	ASTM D1238, condition K		(1)
		$M_n = 16,000$	7	
		$M_n = 19,000$	4	
		$M_n = 25,000$	2	
		$M_n = 39,000$	0.5	
Decomposition temperature	K	TGA	653	(6)
Water absorption	%	293 K, equilibrium	5.8	(1)
Important patents	–	–	–	(3, 4)
Cost	US$ kg^{-1}	–	4–6	
Availability	kg	–	$\sim 1 \times 10^7$	
Suppliers	Mitsubishi Gas Chemical Co., Inc., Tokyo, Japan Solvay & C[ie], Brussels, Belgium			

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Perfluorinated ionomers

RICHARD E. FERNANDEZ

TRADE NAMES Nafion®, Flemion®, Aciplex®

CLASS Chemical copolymers

PREPARATIVE TECHNIQUES 1. Free radical polymerization in fluorocarbon solvents. 2. Aqueous emulsion polymerization.

TYPICAL COMONOMERS

Nafion, Flemion $$CF_2{=}CF{-}O{-}CF_2{-}\underset{\substack{|\\ CF_3}}{CF}{-}O{-}CF_2CF_2SO_2F$$

Aciplex $$CF_2{=}CF{-}O{-}CF_2{-}\underset{\substack{|\\ CF_3}}{CF}{-}O{-}CF_2CF_2CF_2SO_2F$$

Nafion, Aciplex $$CF_2{=}CF{-}O{-}CF_2{-}\underset{\substack{|\\ CF_3}}{CF}{-}O{-}CF_2CF_2CO_2CH_3$$

Flemion $$CF_2{=}CF{-}O{-}CF_2CF_2CF_2CO_2CH_3$$

STRUCTURES

Nafion Sulfonate Resin $${-}(CF_2CF_2)_n{-}\underset{\substack{|\\ CF_2\\ |}}{CFO}{-}CF_2{-}\underset{\substack{|\\ CF_3}}{CFO}{-}CF_2CF_2SO_2F$$

Nafion Carboxylate Resin $${-}(CF_2CF_2)_n{-}\underset{\substack{|\\ CF_2\\ |}}{CFO}{-}CF_2{-}\underset{\substack{|\\ CF_3}}{CFO}{-}CF_2CF_2CO_2CH_3$$

STRUCTURES AFTER HYDROLYSIS

Nafion Sulfonate $${-}(CF_2CF_2)_n{-}\underset{\substack{|\\ CF_2\\ |}}{CFO}{-}CF_2{-}\underset{\substack{|\\ CF_3}}{CFO}{-}CF_2CF_2SO_3H$$

Nafion Carboxylate $${-}(CF_2CF_2)_n{-}\underset{\substack{|\\ CF_2\\ |}}{CFO}{-}CF_2{-}\underset{\substack{|\\ CF_3}}{CFO}{-}CF_2CF_2CO_2H$$

(For commercial materials n varies from about 5–11.)

MAJOR APPLICATIONS Nafion is the DuPont trademark for its family of perfluorinated ionomers, that is, resins and membranes. Asahi Chemical Industry Company produces Aciplex and Asahi Glass Company, Ltd., Japan, produces Flemion; both are competitive products to Nafion in form and function. These perfluorinated ionomers are used in a variety of applications, the largest of which are as an ion exchange resin and in membrane separators in the commercial electrolysis of brine to produce caustic and chlorine. Nafion membranes are also being used in the development of fuel cells and as heterogeneous super acid catalysts in supported, cubed, or powdered form.

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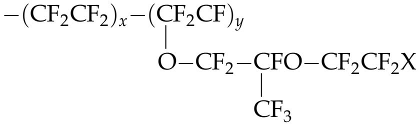
Perfluorinated ionomers

PROPERTIES OF SPECIAL INTEREST The equivalent weight (EW) is a key indicator of the polymer and is defined as the grams of polymer per mole of exchange sites, that is, $-SO_3H$ or CO_2H groups. In other words, EW is the weight in grams of the polymer in acid form that will neutralize one equivalent of base. EW can also be described as the average molecular weight of a repeat unit; for example, one vinyl ether (446) and six TFE units (600) give an EW of 1,046, a typical value for Nafion Sulfonate Resin.

REPEAT UNIT



PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Average molecular weight (of repeat unit)	–	Defines equivalent weight	–	–
Head-to-head contents	%	–	Unknown	–
Degree of branching	%	–	0	–
Typical molecular weight range of polymer	g mol^{-1}	–	1–10 ($\times 10^5$)	(1)
Typical polydispersity index (M_w/M_n)	–	–	Unknown	–
Morphology	Structure of hydrolyzed membranes is generally believed to be of a reverse micelle type, 30–50 Å in size, containing the aqueous ions, acid, and/or salt groups embedded in a continuous fluorocarbon phase.			(2–6)
IR	–	–	–	(7–8)
UV	Transparent down to 200 nm			–
NMR	–	–	–	(9–13)
Solvents	For hydrolyzed sulfonic polymer, aqueous or alcoholic solutions can be made by dissolving the acid form of the polymer at 150–300°C.			(14)
	For hydrolyzed carboxylic polymer, the lithium ion form is preferred and degradation can occur at 250–300°C.			(15)
Swelling	As a function of the solvent, counter ion, EW, and temperature			(16–17)
Solubility parameter	As a measure of the intermolecular forces present			(18)
Solvent effects on molecular motion		–	–	(19)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of fusion	$J g^{-1}$	Depends on EW	5–25	–
Density	$g cm^{-3}$	Unhydrolyzed	2	(20)
		Hydrolyzed	1.4–2.05	
Glass transition temperature	K	Sulfonate, unhydrolyzed	~273	–
		$-SO_3H$ form	376	(21)
		$-SO_3Li$ form	489	(21)
		$-SO_3Na$ form	508	(21)
		$-SO_3K$ form	498	(21)
		$-SO_3Cs$ form	483	(21)
Melting point	K	For unhydrolyzed 1050, depends on EW	523 (typically)	–
Other thermal transitions	–	–	–	(22)
Mechanical properties	–	Sulfonate membranes	–	(23–25)
		Carboxylate membranes	–	(26)
		Both types	–	(27)
Dielectric properties	–	–	–	(28–29)
Electronic conductivity	–	–	–	(30–32)
Permeability coefficient	For oxygen permeation through 700–800 EW Flemion carboxylate membranes			(33)
	Oxygen and hydrogen permeation through Nafion 117 membranes			(34)
Ion and water transport				(35–48)
Water transport				(49–51)
Proton transport		–		(52–55)
		For Dow membranes		(56)
Melt index	g	10 minutes at 270°C using a 1,200 g weight in unhydrolyzed form	5–15 (typically)	–
Biodegradability, effective microorganisms			None known	
Maximum use temperature	K	Atmospheric cell pressure	353–363 (typically)	–
Decomposition temperature	K	Sulfonate in Na^+ form	~673	–
		Carboxylate	~573	
Water absorption	%	Sulfonate in Na^+ form (depending on EW); H^+ form is greater	15–25	(57)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Flammability, flame propagation rate			None	
Cost	US\$ kg^{-2}	Sulfonic resin	2,000	
Availability	Commercially available			
Suppliers	Asahi Chemical Industry Company Asahi Glass Company, Ltd., Japan E. I. DuPont de Nemours and Company, Inc.			

Important Patents

1. ''Process for hydrolysis of fluorinated ion exchange membranes.''	US 5310765	940510
2. ''Preparation of fluorinated copolymers.''	US 5281680	940125
3. ''Ion exchange method and apparatus.''	US 4591439	860527
4. ''Membrane, electrochemical cell, and electrolysis.''	US 4437951	840320
5. ''Process for producing halogen and metal hydroxides with cation exchange membranes of improved permaselectivity.''	US 4030988	770621
6. ''Electrolysis cell using cation exchange membranes of improved permaselectivity.''	US 4026783	770531
7. ''Ion-exchange membrane for brine electrolysis.''	US 4666574	870519

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Phenolic resins

MILIND SOHONI

ALTERNATIVE NAMES Novolacs, resoles

TRADE NAME Bakelite (Georgia Pacific Resins, Inc.)

CLASS Thermoset polymers; chemical copolymers

TYPICAL COMONOMERS Phenols, substituted phenols, formaldehyde

POLYMERIZATIONS Condensation

MAJOR APPLICATIONS Construction materials, electronics, aerospace, molded parts, insulating varnishes, laminated sheets, industrial coatings, wood bonding, fiber bonding, and plywood adhesives.

PROPERTIES OF SPECIAL INTEREST Toughness, temperature resistance, low void content, chemical resistance, and corrosion inhibition.

Substituted phenols used for phenolic resins[1]

Substituted phenol	Resin application
Cresol (*o*-, *m*-, *p*-)	Coatings, epoxy hardners
p-*t*-Butylphenol	Coatings, adhesives
p-Octylphenol	Carbonless paper, coatings
p-Nonylphenol	Carbonless paper, coatings
p-Phenylphenol	Carbonless paper
Bisphenol A	Low color molding compounds, coatings
Resorcinol	Adhesives
Cashew nutshell liquid	Friction particles

Forms of formaldehyde used in phenolic resin synthesis[1]

		Resin preparation	
Type	Chemical formula	Advantages	Disadvantages
Gaseous formaldehyde	CH_2O	–	Unstable
Formalin			
36%	$HO(CH_2O)_nH$, $n \approx 2$	Easy handling, moderate reactivity, stable at RT	High water content
50%	$HO(CH_2O)_nH$, $n \approx 3$	Increased capacity	Elevated temp. storage, formic acid formation
Paraformaldehyde	$HO(CH_2O)_nH$, $n \approx 20$–100	Increased capacity, water free	Dangerously high reactivity, solids handling
Trioxane	$(CH_2O)_3$	Water-free	Catalyst requirements, cost
Hexamethylenetetramine	$(CH_2)_6N_4$	Autocatalytic	Amine incorporation

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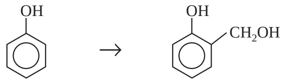
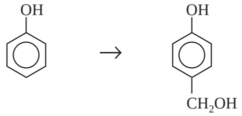
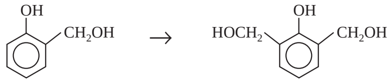
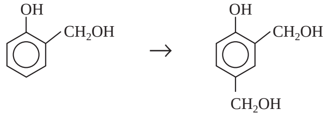
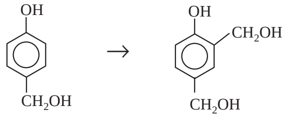
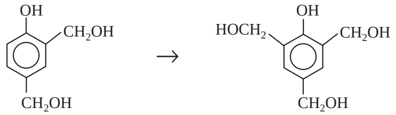
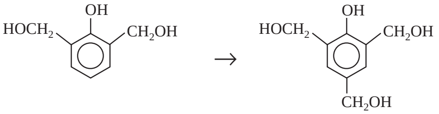
Relative rate constants for methylolation of phenol

Rate constant	Ref. (2)	Ref. (3)	Ref. (4)
	1.00	1.00	1.00
	1.18	1.09	1.46
	1.66	1.98	1.75
	1.39	1.80	3.00
	0.71	0.79	0.85
	1.73	1.67	2.04
	7.94	3.33	4.36

Methylene group distribution, % in resoles[1]

	Catalyst	
Methylene group	NaOH	Hexamethylenetetramine (6 pph)
2-CH_2OH	30	24
2-CH_2OCH_2OH	24	1
2-CH_2OR	2	4
4-CH_2OH	12	9
4-CH_2OCH_2OH	16	0
4-CH_2OR	2	4
$2,2'$-CH_2	0	0
$2,4'$-CH_2	7	12
$4,4'$-CH_2	7	10
2-CH_2N	0	27
4-CH_2N	0	7
Benzoxazine	0	2

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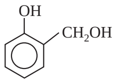
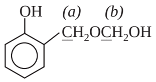
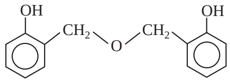
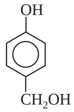
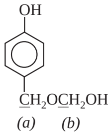
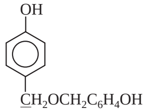
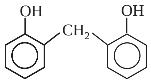
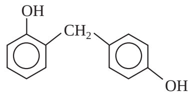
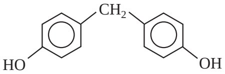
Proton NMR chemical shifts of methylene groups in phenolic resins[5]

Methylene group	Chemical shift* (ppm)
2-CH_2OH	5.1
2-CH_2OR	5.0
4-CH_2OH	4.8
4-CH_2OR	4.7
2, 2′-CH_2	4.2
2, 4′-CH_2	4.1
4, 4′-CH_2	3.8
2-CH_2N	4.0
4-CH_2N	3.5

*10% concentration in d_5-pyridine.

Chemical shifts of methylene carbons in liquid resoles[1]

Structure*		Chemical shift† (ppm)
Methylol C in		61.3
		(a) 65.4 (b) 88.0
Benzyl C in		68.9
Methylol C in		63.8
		(a) 68.5 (b) 88.0
		71.5
Methylene C in		31.5
Methylene C in		35.0
Methylene C in		40.4

*Designated carbon is shown underlined or described.
†From tetramethylsilane in d_6-acetone solution.

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Phenolic resins used in coatings[1]

Property	Unsubstituted phenol		Substituted phenol	
	Heat-reactive	Non-heat-reactive	Heat-reactive	Non-heat-reactive
Type	Phenol	Phenol	Cresol *p*-*t*-Butyl phenol Bisphenol A	Cresol *p*-*t*-Butyl phenol Bisphenol A
Formaldehyde ratio	F > P	P > F	F > P	P > F
Catalyst	Alkaline	Acid	Alkaline	Acid
Stability	Low	High	Low	High
Softening point	Low	High	Low	High

Strength properties of phenolic-carbon-fiber composites[1]

Property	Units	Resin (%)		
		Phenolic		Epoxy novolak, 27
		40	35	
Tensile strength	MPa*	115	63	64
Flexural strength	MPa*	183	126	110
Flexural modulus	GPa†	15.8	6.3	6.4

*To convert MPa to psi, multiply by 145.
†To convert GPa to psi, multiply by 145,000.

Functionality versus number of phenol alcohols[6]

Phenol	Functionality of phenol	Number of mono-alcohols	Number of di-alcohols	Number of tri-alcohols	Number of tetra-alcohols	Total number of alcohols
2,4-Dimethylphenol	1	1	–	–	–	1
2,6-Dimethylphenol	1	1	–	–	–	1
p-Cresol	2	1	1	–	–	2
o-Cresol	2	2	1	–	–	3
2,3-Dimethylphenol	2	2	1	–	–	3
2,5-Dimethylphenol	2	2	1	–	–	3
3,4-Dimethylphenol	2	2	1	–	–	3
3,5-Dimethylphenol	3	2	2	1	–	5
Phenol	3	2	2	1	–	5
Resorcinol	3	2	2	1	–	5
m-Cresol	3	3	3	1	–	7
Hydroquinone	4	1	3	1	1	6
Catechol	4	2	3	2	1	8

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First-order rate constants and comparative rates of reaction for various phenols[7]

Phenol	Apparent first-order rate constant	Relative reactivity
3,5-Xylenol	0.0630	7.75
m-Cresol	0.0233	2.88
2,3,5-Trimethylphenol	0.0121	1.49
Phenol	0.00811	1.00
3,4-Xylenol	0.00673	0.83
2,5-Xylenol	0.00570	0.71
p-Cresol	0.00287	0.35
Saligenin	0.00272	0.34
o-Cresol	0.00211	0.26
2,6-Xylenol	0.00130	0.16

Properties of phenol-formaldehyde molding compounds[8]

Property	Units	Phenol-formaldehyde, wood flour and cotton floe
Pigmentation and coloring possibilities	–	Limited
Appearance	–	Opaque
Molding qualities	–	Excellent
Type of resin	–	Thermosetting
Molding temperature	°F (°C)	290–380 (143–193)
Molding pressure	psi	2,000–4,000
Mold shrinkage	in in^{-1}	0.004–0.009
Specific gravity	–	1.32–1.45
Tensile strength	psi	$6.5–9 \times 10^3$
Flexural strength	psi	$8.5–12 \times 10^3$
Notched Izod impact strength	ft-lb in^{-1}	0.24–0.6
Rockwell hardness	–	M 96–M 120
Thermal expansion	$°C^{-1}$	$3.0–4.5 \times 10^{-5}$
Deflection temperature under load	°F	260–340
Dielectric strength, short time, 0.125 in thickness	V mil^{-1}	200–425
Dielectric constant	–	4.0–7.0
Dissipation factor	–	0.03–0.07
Arc resistance	s	Tracks
Cold-water absorption, room temperature		
24 h, 0.125 inch thickness	%	0.3–1.0
7 days	mg $(100\ cm^2)^{-1}$	200–750
Boiling water test, 10 min, 100°C	%	0.4–1.0
Burning rate	–	Very low
Effect of sunlight	–	General darkening

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Properties of phenol-formaldehyde laminates[8]

Properties	Units	Phenol-formaldehyde laminate	
		Paper-base filler	Glass fabric base
Coloring possibilities	—	Limited	Limited
Appearance	—	Opaque	Opaque
Laminating temperature	°F	275–350	275–350
Laminating pressure	psi	1,000–1,800	1,500–2,000
Specific gravity	—	1.28–1.4	1.4–1.9
Tensile strength	psi	$8–20 \times 10^3$	$9–50 \times 10^3$
Flexural strength	psi	$10.5–30 \times 10^3$	$16–80 \times 10^3$
Notched Izod impact strength	ft-lb in^{-1}	0.3–1.0	4–18
Rockwell hardness	—	M 70–M 120	M 105–M 110
Water absorption, 24 h, room temperature, 0.125 inch thickness	%	0.2–4.5	0.3–1.5
Effect of sunlight	—	General darkening and lower surface resistance	General darkening and lower surface resistance
Machining qualities	—	Fair to excellent	Fair to good
Thermal expansion	$°C^{-1}$	$1.4–3.0 \times 10^{-5}$	$1.5–2.5 \times 10^{-5}$
Resistance to heat (continuous)	°F	225–250	250–500
Heat-distortion temperature	°F	250–over 320	Over 320
Burning rate	—	Very low	Nil
Dielectric strength, short time	V mil^{-1}	300–1,000	300–700
Dielectric constant, at 10^6 cps	—	3.6–6.0	3.7–6.0
Dissipation factor, at 10^6 cps	—	0.02–0.08	0.005–0.05
Arc resistance	s	Tracks	Tracks

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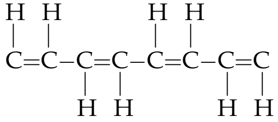
Polyacetylene

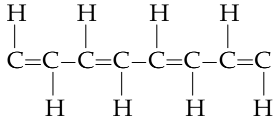
SHUHONG WANG AND PING XU

CLASS Conjugated and other unsaturated polymers

STRUCTURE *cis*-Polyacetylene



trans-Polyacetylene



MAJOR APPLICATIONS Power cable sheathing, prime conductor, energy load leveling systems, batteries, and signal processing devices.

PROPERTIES OF SPECIAL INTEREST Insulating, semiconducting, conducting, and nonlinear optical properties.

POLYMERIZATION Solvent evacuation (SE) method and intrinsic nonsolvent (INS) method.

Thermal behavior[1]

Cis isomer
1. *Cis* to *trans* isomerization at 145°C
2. Molecular rearrangement at 325°C
3. Thermal decomposition at 420°C

Unit cell dimensions

Isomer	Lattice	Cell dimensions (Å) *a*	*b*	*c*	Reference
Cis	Orthorhombic	7.61	4.47	4.39	(2–5)
Trans	Orthorhombic	7.32	4.24	2.46	(6–8)

PROPERTY	UNITS	CONDITIONS	*CIS* VALUE	*TRANS* VALUE	REFERENCE
Tensile strength	MPa	SE polyacetylene	600	900	(9)
		INS polyacetylene	800	2,100	
Tensile elongation	%	SE polyacetylene	6–8	–	(9)
		INS polyacetylene	6–9	–	
Tensile modulus	MPa	SE polyacetylene	30–40	100	(9)
		INS polyacetylene	28	40	

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PROPERTY	UNITS	CONDITIONS	*CIS* VALUE	*TRANS* VALUE	REFERENCE
Cis content	%	SE polyacetylene	70–90	–	(9)
		INS polyacetylene	85–95	–	
Density	g cm^{-3}	SE and INS polyacetylene	1.0–1.15	1.0–1.15	(9)
Magic angle spinning ^{13}C NMR	ppm	Solid-state	127–128	136–137	(10)
Linear absorption coefficient	cm^{-1}	Reflection method: *cis* at 18,500 cm^{-1}; *trans* at 15,400 cm^{-1}	1.4×10^5	1.5×10^5	(11)
Absorption edge	eV	–	1.90	1.35	(12)
Thermal activation energy	eV	–	0.6	0.3	(12)
Dark conductivity	$(W\ cm)^{-1}$	–	2×10^{-9}	5×10^{-6}	(12)
Electrical conductivity	S cm^{-1}	Doping species			(13)
		None	1.9×10^{-9}	4.4×10^{-5}	
		I_2	360	160	
		AsF_5	560	400	
		IBr	400	120	
		$NaC_{10}H_8$	25	80	
		$MoCl_5$	200	–	
		WCl_6	200	–	
		$PtCl_4$	134	–	
		$RhCl_3$	6×10^{-4}	–	
		$CuCl_2$	2×10^{-3}	–	
		$InCl_3$	600	–	
		$LiAlH_4$	–	6	

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Polyacrylamide

ROBERT A. ORWOLL AND YONG S. CHONG

ACRONYM; CHEMICAL ABSTRACTS NAME AND NUMBER; TRADE NAME PAAm; 2-propenamide homopolymer [9003-05-08]; Cyanamer (American Cyanamid)

CLASS Vinyl polymers

STRUCTURE $[-CH_2-\underset{\displaystyle CONH_2}{\underset{|}{C}}H-]$

MAJOR APPLICATIONS Flocculants in water treatment, paper manufacture, mining, and oil recovery; absorbents; gels for electrophoresis.

PROPERTIES OF SPECIAL INTEREST Amorphous. High affinity for water and completely miscible in water. Low toxicity. Low cost.

POLYMERIZATION CONDITIONS Free-radical polymerizations of acrylamide in aqueous solutions and solid-state polymerization of crystalline acrylamide with ionizing radiation.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	71.08	–
Tacticity (stereoregularity)	–	Reaction conditions: temp. = 70°C; monomer conc. = 16 wt% in water; initiator = $(NH_4)_2S_2O_8$; chain-transfer agent = isopropanol	Probability meso $P_m = 0.43$	(1)
Head-to-head contents	–	Reaction conditions: temp. = 25°C; monomer conc. = 10% in water; initiators (25 mg/100 ml) = $K_2S_2O_8$, $Na_2S_2O_5$	Head-to-head units = 4.5%	(2)
IR spectrum	–	–	–	(3, 4)
Raman spectrum	–	–	–	(5)
NMR	–	^{13}C spectrum, 100 MHz	–	(1)
Solvents	Water, ethylene glycol, formamide, hydrazine			(6)
Nonsolvents	Methanol, hydrocarbons, and other common organic liquids			(6)
Partial specific volume ($\partial V/\partial m_2$)	$cm^3\,g^{-1}$	20°C, water	0.696	(7)
		25°C, water	0.716	(8)
		25°C, water	0.693 ± 0.002	(9)
		25°C, water	0.674	(10)
		20°C, water/methanol (3:2 v/v)	0.655	(10)
		0.1 M NaCl (aq.)	0.702	(11)

PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Apparent adiabatic compressibility in solution	$cm^3\ bar^{-1}\ g^{-1}$	25°C, water			-4.2×10^{-6}	(8)
Theta temperature Θ	K	Water (extrapolated value)			235	(12)
		Water/methanol (3:2 v/v), $0.33 < M_w \times 10^{-4} < 81$			293	(10)
		Water/methanol (59:41 v/v), $92 < M_w \times 10^{-4} < 820$			294	(13)
		Water/methanol (59:41 v/v), $43 < M_w \times 10^{-4} < 1{,}000$			298	(14)
Interaction parameter χ	–	Solvent	Temp. (°C)	$M \times 10^{-6}$ (g mol^{-1})		
		Water	25	0.43	0.44	(12)
		Water	60	0.43	0.42	(12)
		Water	25	0.107	0.495	(9)
Enthalpy parameter χ_H	–	Solvent	Temp. (°C)	$M \times 10^{-6}$ (g mol^{-1})		
		Water	25	0.43	0.22	(12)
		Water	60	0.43	0.20	(12)
		Water	25	0.107	0.08 ± 0.008	(9)
Second virial coefficient A_2	mol cm^3 g^{-2} ($\times 10^4$)	Solvent	Temp. (°C)	$M \times 10^{-6}$ (g mol^{-1})		
		Water	20	0.25	3.1	(7)
		Water	20	2.4	2.9	(7)
		Water	20	11	2.2	(7)
		Water	25	0.43	4.4	(14)
		Water	25	4.7	0.64	(15)
		Water	25	0.5–6	4 ± 2	(16)
		Water	25	0.11	1.4	(9)
		Water	25	10	1.7	(14)
		0.1 M NaCl (aq.)	–	6	2.5 ± 0.4	(11)
		1 M NaCl (aq.)	–	5.5	2.7	(11)
		4 M NaCl (aq.)	–	5.5	2.9	(11)
		0.1 M LiCl	–	6.8	1.9	(11)
		Water/methanol (3:2 v/v)	20	0.77	0.008	(10)
		Ethylene glycol	25	0.5–5	0.27 ± 0.08	(16)
		Formamide	–	6.8	1.3	(11)

Mark-Houwink parameters: *K* and *a*

Solvent	Temp. (°C)	$M \times 10^{-6}$ (g mol^{-1})	$K \times 10^2$ (with [η] in ml g^{-1})	*a*	Reference
Water	20	0.25–3	3.09	0.67	(7)
Water	25	0.5–6	0.49	0.8	(16)
Water	25	0.038–9	1.00	0.755	(6)
Water	25	0.01–0.36	6.8	0.66 ± 0.05	(17)

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Solvent	Temp. (°C)	$M \times 10^{-6}$ (g mol^{-1})	$K \times 10^2$ (with [η] in ml g^{-1})	a	Reference
Water	25	0.003–0.8	1.83	0.72	(18)
Water	25	0.43–10	0.742	0.775	(14)
Water	30	0.02–0.5	0.631	0.80	(19)
Water	30	0.04–1.3	0.65	0.82	(20)
0.1 M NaCl (aq.)	—	0.2–8	0.933	0.75	(11)
0.2 M NaCl (aq.)	20	0.25–3	3.02	0.68	(7)
0.5 M NaCl (aq.)	25	0.5–6	0.719	0.77	(16)
1.0 M NaCl (aq.)	20	0.25–3	2.88	0.69	(7)
10% NaCl (aq.)	25	0.43–10	0.81	0.78	(14)
1.0 M $NaNO_3$ (aq.)	30	0.5–3	3.73	0.66	(6)
Water/methanol (3:2 v/v)	20	0.006–0.8	0.127	0.50	(10)
Water/methanol (59:41 v/v)	25	0.43–10	15	0.50	(14)
Ethylene glycol	25	0.5–5	13.6	0.54	(16)
Formamide	25	0.5–6	1.27	0.74	(21)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Huggins constant k'	—	0.5 M NaBr (aq.)	0.46	(22)
		20°C	See table below	(7)

$M_w \times 10^{-6}$ (g mol^{-1})	Huggins constant k'		
	Water	0.2 M NaCl (aq.)	1.0 M NaCl (aq.)
0.26	0.41	0.38	0.38
0.62	0.40	0.41	0.37
1.0	0.28	0.40	0.36
2.4	0.17	0.34	0.37
2.8	0.39	0.38	0.39
11	0.37	0.40	0.35

PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Sedimentation constant S_0	s^{-1} ($\times 10^{13}$)	Solvent	Temp. (°C)	$M \times 10^{-6}$ (g mol^{-1})		(16)
		0.5 M NaCl (aq.)	20	0.8–6	$0.09\, M_w^{0.32}$	
Characteristic ratio $\langle r^2 \rangle / nl^2$ ($l = 0.154$ nm)		Solvent	Temp. (°C)	$M \times 10^{-6}$ (g mol^{-1})		
		Water	25	0.5–6	$3.6\, M_w^{0.18}$	(16)
		0.1 M NaCl (aq.)	—	0.8–8	$49\, M_w^{0.28}$	(11)
		Water/methanol (3:2 v/v), Θ solvent	20	0.08–0.8	9.3	(18)

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Polyacrylamide

PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Characteristic ratio $\langle r^2 \rangle / nl^2$ ($l = 0.154$ nm)		Solvent	Temp. (°C)	$M \times 10^{-6}$ ($g\,mol^{-1}$)		
		Water/methanol (59:41 v/v), Θ solvent	25	0.43–10	11.3	(14)
		Salt/water/methanol (?:59:41 v/v), Θ solvent	21	0.9–8	14	(13)
		Ethylene glycol	25	0.5-6	$21\,M_w^{0.02}$	(16)
Glass transition temperature T_g	K	—			461	(22)
Softening temperature	K	—			481	(23)

Refractive index increment dn/dc

Solvent	Temp (°C)	dn/dc ($cm^3\,g^{-1}$)			Reference
		$\lambda = 436$ nm	$\lambda = 546$ nm	λ not reported	
Water	20	0.185	0.182	—	(7)
Water	25	—	0.187	—	(16)
Water	25	—	0.189	—	(14)
Water	20–60	—	0.149	—	(12)
Water	—	—	—	0.165	(11)
0.1 M LiCl (aq.)	—	—	—	0.164	(11)
0.1 M NaCl (aq.)	—	—	—	0.165	(11)
0.2 M NaCl (aq.)	20	0.186	0.182	—	(7)
1 M NaCl (aq.)	—	—	—	0.159	(11)
1 M $Mg(ClO_4)_2$ (aq.)	25	—	0.174	—	(10)
Ethylene glycol	25	—	0.095-0.105	—	(16)
Formamide	—	—	—	0.095	(11)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Critical surface tension γ_c	$mN\,m^{-1}$	20°C, contact angle method	52.3	(24)
Water absorption (residual wt% water)	%	Dried under vacuum at 20°C	15	(25)
		Dried overnight under vacuum at 60–80°C	7–11	(7)
		Dried overnight under vacuum at 60–80°C, then 4 h at 120°C	~0	(7)
		Dried under vacuum for 24 h at 25°C	3	(16)
		Dried under vacuum for 24 h at 25°C, then 9 h at 50°C	0.9	(16)
		Dried under vacuum for 24 h at 25°C, then 9 h at 50°C, then 7 h at 110°C	~0	(16)

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Poly(acrylic acid)

ROBERT A. ORWOLL AND YONG S. CHONG

ACRONYMS; CHEMICAL ABSTRACTS NUMBER; TRADE NAMES PAA, PAAc; [9003-01-4]; Acrysol, Acumer, Acusol, Duolite (Rohm & Haas); Alcogum, Alcosperse, Aquatreat (Alco); Carbopo, Good-ritel (B F Goodrich); Sokalan (BASF)

CLASS Vinyl polymers

STRUCTURE $[-CH_2-CH(COOH)-]$

MAJOR APPLICATIONS Thickening and suspension agents for petroleum recovery, pigment dispersements in paint, ion exchange resins (with cross-linking), flocculating agents for particles suspended in water, adhesives. Many applications involve copolymers of acrylic acid.

PROPERTIES OF SPECIAL INTEREST Amorphous polymers.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	72.06	–
IR spectrum	–	–	–	(1)
Density	$g\,cm^{-3}$	–	1.22	(2)
Solvents	Water, dioxane, ethanol, dimethylformamide, methanol			(3)
Nonsolvents	Acetone, diethyl ether, benzene, aliphatic hydrocarbons			(3)
Partial specific volume	$cm^3\,g^{-1}$	Water, 25°C	0.648	(4)
Apparent adiabatic compressibility in solution	$cm^3\,bar^{-1}\,g^{-1}$	25°C, water	1.2×10^{-6}	(4)
		25°C, PAAc 25% neutralized with NaOH, water	-18×10^{-6}	
		25°C, PAAc 100% neutralized with NaOH, water	-54×10^{-6}	
		25°C, PAAc 25% neutralized with NaOH, 1.0 M NaCl (aq.)	-53×10^{-6}	
Theta temperature Θ	K	Dioxane	303 ± 1 (LCST)	(5)
		Water, 1.245 M in NaCl, and enough NaOH to neutralize 1/3 of acid groups	305 ± 3 (UCST)	(5)
		0.2 M HCl (aq.)	287	(6)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Interaction parameter χ	—	0.2 M HCl (aq.); $M_v = 0.43 \times 10^6$ g mol^{-1}		(6)
		20°C	0.498	
		68°C	0.490	
Enthalpy parameter χ_H	—	Water; $M = 0.43 \times 10^6$ g mol^{-1}		(6)
		20°C	0.0631	
		68°C	0.0542	
Second virial coefficient A_2	mol cm^3 g^{-2}	0.2 M HCl (aq.); 20–68°C; $M_v = 0.43 \times 10^{-6}$ g mol^{-1}	$49.9(1–287\ K/T)$	(6)
Mark-Houwink parameters: K and a	K = ml g^{-1} (with $[\eta]$) a = None	1,4-Dioxane; 30°C; M = 0.13–0.82 ($\times 10^6$) g mol^{-1}	$K = 8.5 \times 10^{-2}$ $a = 0.50$	(7)
Huggins constant k'	—	1,4-Dioxane, 30°C	0.25–0.30	(3)
		0.5 M NaBr (aq.)	0.30	(8)
Characteristic ratio $\langle r^2 \rangle / nl^2$ (l = 0.154 nm)	—	1,4-Dioxane; 30°C; M = 0.13–0.82 ($\times 10^6$) g mol^{-1}	9.0 ± 0.5	(7)
Glass transition temperature T_g	K	—	376	(9)
			379 ± 2	(10)
			399	(8)
Refractive index increment dn/dc	cm^3 g^{-1}	1,4-Dioxane, 25°C, $\lambda = 436$ nm	0.089	(7)
		0.2 M HCl (aq.), 20–60°C, $\lambda = 546$ nm	0.146	(6)
Water absorption (wt% water)	%	30°C, 32% relative humidity	4.8	(10)
		30°C, 54% relative humidity	7.7	
		30°C, 69% relative humidity	13.7	

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Poly(acrylonitrile)

ANTHONY L. ANDRADY

TRADE NAME Barex (copolymer)

CLASS Acrylic polymers

STRUCTURE $[-CH_2CHCN-]$

MAJOR APPLICATIONS Acrylonitrile copolymers are used extensively in textile fiber manufacture and in nitrile rubber. Copolymers are used in gaskets, grommets, hoses, printing roll surfaces, diaphragms, and in plumbing accessories. They also are used in adhesive and coating applications.

PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Preparative techniques	Radical polymerization:				
	Bulk polymerization using conventional initiators (AIBN, peroxides) at < 100°C				(1)
	Continuous slurry process				(2)
	Emulsion polymerization				(3)
Typical comonomers	Vinylidene chloride, 4-vinyl pyridine, styrene, butadiene and styrene				(4)
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–		53.06	–
IR	FTIR study of the homopolymer and its thermal degradation				(5–7)
NMR	^{13}C NMR of homopolymer in 20 wt%				(8)
	DMSO at 50°C				(9, 10)
Solvents	Dioxanone, ethylene carbonate, DMSO, chloroacetonitrile, dimethyl phosphite, dimethyl sulfone, sulfuric acid, nitric acid, DMF				(11–15)
Nonsolvents	Hydrocarbons, chlorinated hydrocarbons ketones, diethyl ether, acetonitrile				(12, 13)
Second virial coefficient A_2	$mol\,cm^3\,g^{-2}$ ($\times 10^4$)	Temp. (°C)	M_n		
		20	98–120	22.9–21.4	(16, 17)
			9–69	32.2–7.0	(16)
		25	43–298	21	(16, 18)
			27–159	16–20	(16, 19)
		25–40	35–101	19.1	(16, 20)

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Mark-Houwink parameters: K and a	K = ml g^{-1} a = None	Butyrolactone	$K \times 10^3$	a	(21)
		20°C	34.3	0.730	
		30°C	57.2	0.67	
		30°C	34.2	0.70	
		30°C	40.0	0.69	
		DMF, 20°C	30.7	0.76	(22)
Unit cell dimensions	Å	Orthorhombic	$a = 10.55$, $b = 5.8$, $c = 5.08$		(23)
			$a = 21.2$, $b = 11.6$, $c = 5.04$		(24)
			$a = 18.1$, $b = 6.12$, $c = 5.00$		(25)
Heat of fusion	kJ mol^{-1}	–	5.021		(26, 27)
Entropy of fusion	kJ mol^{-1}	–	0.0085		(26, 27)
Glass transition temperature	K	Dielectric, 1 Hz	398		(28)
		Calorimetry	370		(29)
Melting transition temperature	K	Calorimetry	593		(30)
		Calorimetry (40°C min^{-1} heating rate)	599		(31)
Heat capacity	kJ K^{-1} mol^{-1}	100°C	0.0302		(32)
		200°C	0.0493		
		300°C	0.0688		
		370°C	0.0862		
Tensile strength	MPa	Styrene-acrylonitrile copolymers: % Acrylonitrile			(33)
		27	72.47		
		21	63.85		
		14	57.37		
		9.8	54.61		
		5.5	42.27		
Elongation	%	Styrene-acrylonitrile copolymers: % Acrylonitrile			(33)
		27	3.2		
		21	2.5		
		14	2.2		
		9.8	2.1		
		5.5	1.6		

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric constant (film)	—	Frequency (Hz)		(34)
		10^6	4.2	
		10^3	5.5	
		60	6.5	
Dissipation factor	—	Frequency (Hz)		(34)
		10^6	0.033	
		10^3	0.085	
		60	0.113	
Permeability coefficient P	$m^3(STP)m\ s^{-1}\ m^{-2}$ Pa^{-1} ($\times 10^{-9}$)	Unplasticized film, 25°C		(35)
		O_2	0.00015	
		CO_2	0.00060	
		H_2O	230	
Pyrolyzability	Thermal degradation and cyclization of homopolymer and copolymers			(5, 36)
Thermal conductivity	$W\ m^{-1}\ K^{-1}$	293°C	0.26	(37, 38)

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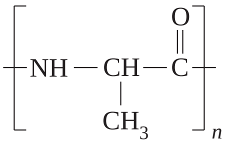
Poly(L-alanine)

DOUGLAS G. GOLD AND WILMER G. MILLER

CLASS Polypeptides and proteins

STRUCTURE



MAJOR APPLICATIONS Serves as a model for various proteins.

PROPERTIES OF SPECIAL INTEREST Two crystalline forms of poly(L-alanine), the α-helix and β-sheet, have been observed.[1]

SYNTHESIS Similar to the synthesis of poly(γ-benzyl-L-glutamate) (see the entry on *Poly(γ-benzyl-L-glutamate)* in this handbook); involves the conversion of the amino acid to the N-carboxyanhydride (NCA) monomer by reaction with phosgene gas followed by polymerization of the NCA with an appropriate initiator (e.g., *n*-butyl amine). Typical comonomers include other amino acid NCAs.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\ mol^{-1}$	–	71	–
Typical molecular weight range	$g\ mol^{-1}$	–	<50,000	–
IR (characteristic absorption frequencies)	cm^{-1}	α-helix β-sheet	1,657; 2,930; 2,985; 3,293 1,634; 2,930; 2,985; 3,283	(2)
NMR	–	–	–	(3)
Solvents	–	25°C	Dichloroacetic acid (DCA), tri-fluoroacetic acid (TFA), phosphoric acid, mixed solvents containing TFA	(4, 5)
Nonsolvents	–	–	Water	–
Second virial coefficient	$mol\ cm^3\ g^{-2}$	DCA, 25°C, 1.6×10^4	5×10^{-3}	(6)
Characteristic ratio	–	DCA, 25°C	5.3–5.6	(6)
Persistence length	Å	DCA, 25°C	44	(7)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density (crystalline)	$g\,cm^{-3}$	α-helix β-sheet	1.25 1.34–1.37	(8)
Optical activity $[m']_D$	–	99% $CHCl_3$, 1% DCA TFA	$[m']_D + 21$ $[m']_D - 90$	(8)
Surface tension	$mN\,m^{-1}$	20°C	45.2	(8)
Helix pitch	Å	α-helix	5.41	(1)
Axial translation per residue	Å	α-helix	1.496	(1)
Cost	US$ g^{-1}	25 mg – 1 g	110	–
Availability	g	–	0.025–1	–
Suppliers	Sigma Chemical Co., P.O. Box 14508, St. Louis, Missouri 63178, USA. Aldrich Chemical Co., Inc., 1001 West Saint Paul Avenue, Milwaukee, Wisconsin 53233 USA.			

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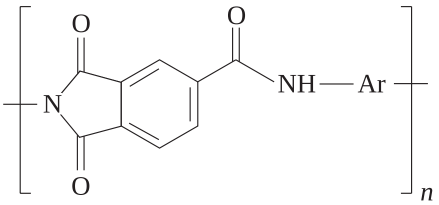
Poly(amide imide)

LOON-SENG TAN

ACRONYM, TRADE NAMES PAI, Torlon®, Amoco-AI-10

CLASS Polyimides; engineering thermoplastics

STRUCTURE



(Ar = aromatic bridging group)

SYNTHESIS Poly(amide imides) can be prepared via the following methods: (a) two-step polycondensation of trimellitic anhydride and aromatic amines;[1,2] (b) low temperature polymerization of trimellitic anhydride-based diacid chlorides and aromatic amines;[3] (c) polycondensation of trimellitic anhydride or dicarboxylic acids derived from trimellitic anhydride with aromatic diisocyanates;[4] and (d) direct polycondensation of dicarboxylic acids derived from trimellitic anhydride and aromatic amines via Yamazaki-Higashi reaction.[5]

MAJOR APPLICATIONS A wide variety of injection-molded automotive parts such as housings, connectors, switches, relays, thrust washers, spline liners, valve seats, bushings, piston rings and seals, wear rings, ball bearings, rollers, thermal insulators, etc.; laminated parts such as printed circuit boards, honeycomb core, radomes, etc.

PROPERTIES OF SPECIAL INTEREST Commercial poly(amide imide) (Torlon) is melt-processable and injection-moldable either in neat form or with reinforcing fillers such as glass fiber, graphite fiber, and combinations of these with polyfluorocarbon and with TiO_2. Parts fabricated from Torlon have excellent frictional properties, and can be used without lubrication in many applications.

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Commercial poly(amide imide) products*

Product name	Product description
Torlon 4000T	Unfilled poly(amide imide) powder for adhesive applications
Torlon high strength grades	High-strength grades perform more like metals at elevated temperature and are recommended for repetitively-used precision mechanical and load-bearing parts
	4203L contains 3% TiO_2 and 0.5% fluorocarbon
	5030 contains 30% glass fiber and 1% fluorocarbon
	7130 contains 30% graphite fiber and 1% fluorocarbon
	7330 is a proprietary blend of carbon fiber and fluorocarbon
Torlon wear resistant grades	4347 contains 12% graphite powder and 8% fluorocarbon
	4301 contains 12% graphite powder and 3% fluorocarbon
	4275 contains 20% graphite powder and 3% fluorocarbon
AMOCO-AI-10	Poly(amide imide) powder composed of about 50% of amic acid form

*Supplier: Amoco Polymers, Inc., 4500 McGinnis Ferry Road, Alpharetta, Georgia 30202-3914.

Typical mechanical properties of unfilled Torlon 4000T

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	ASTM D792	1.380	(6)
Tensile strength, break	MPa	ASTM D638, 23°C	117.2	(7)
Tensile modulus	MPa	ASTM D638, 23°C	5,200	(7, 6)
Elongation, break	%	ASTM D638, 23°C	10–18	(7, 6)
Flexural strength, yield	MPa	ASTM D790, 23°C	189.0	(7, 6)
Flexural modulus	MPa	ASTM D790	3,590	(7, 6)
Compressive strength	MPa	ASTM D695, 23°C	241.4	(7, 6)
Impact strength, notched Izod	$J\,m^{-1}$	ASTM D256, 23°C, 3.2 mm	136	(7, 6)
Impact strength, unnotched Izod	$J\,m^{-1}$	ASTM D256, 23°C, 3.2 mm	1,088	(6)
Hardness, Rockwell E	–	–	78	(7)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	ASTM C177	0.24	(7)
Linear thermal expansion coefficient	K^{-1}	ASTM D696, (cm/cm)	3.60×10^{-5}	(7, 6)
Deflection temperature	K	ASTM D648, at 1.81 MPa	525–533	(7, 6)
Volume resistivity	ohm m	ASTM D257	3.0×10^{13}	(7)
Surface resistivity	ohm	ASTM D257	$>1.0 \times 10^{17}$	(7)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric strength	$kV\,mm^{-1}$	ASTM D149	17.3	(7)
Dielectric constant	–	ASTM D150, at 106 Hz	4.0	(7)
Dissipation factor	–	ASTM D150, at 106 Hz	0.009	(7)

Mechanical properties of Torlon 4203L*

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength	MPa	ASTM D1708		(8, 9)
		−196°C	218	
		23°C	192	
		135°C	117	
		232°C	66	
Tensile elongation	%	ASTM D1708		(8, 9)
		−196°C	6	
		23°C	15	
		135°C	21	
		232°C	22	
Tensile modulus	MPa	ASTM D1708, 23°C	4,900	(8, 9)
Flexural strength	MPa	ASTM D790		(8, 9)
		−196°C	287	
		23°C	244	
		135°C	174	
		232°C	120	
Flexural modulus	MPa	ASTM D790		(8, 9)
		−196°C	7,900	
		23°C	5,000	
		135°C	3,900	
		232°C	3,600	
Compressive strength	MPa	ASTM D695, 23°C	220	(8, 9)
Compressive modulus	MPa	ASTM D695, 23°C	4,000	(8, 9)
Shear strength	MPa	ASTM D732, 23°C	128	(8, 9)
Impact strength, notched Izod	$J\,m^{-1}$	ASTM D256, 23°C, 3.2 mm	142	(8, 9)
Impact strength, unnotched Izod	$J\,m^{-1}$	ASTM D256, 23°C, 3.2 mm	1,062	(8, 9)
Poisson's ratio	–	–	0.45	(8, 9)

* Filler contents: 3% TiO_2; 0.5% fluorocarbon.

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Thermal properties of Torlon 4203L*

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Deflection temperature	K	ASTM D648, at 1.8 Mpa	551	(8, 9)
Linear thermal expansion coefficient	K^{-1}	ASTM D696, (cm/cm)	30.6×10^{-6}	(8, 9)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	ASTM C177	0.26	(8, 9)

* Filler contents: 3% TiO_2; 0.5% fluorocarbon.

Flammability data of Torlon 4203L*

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Limiting oxygen index	%	ASTM D2863	45	(8, 9)
FAA smoke density (minimum light transmittance)	%	National Bureau of Standards, NFPA 258, specimen thickness = 1.3–1.5 mm	92 (smoldering) 6 (flaming)	(8, 9)
Maximum specific optical density D_m	—	National Bureau of Standards, NFPA 258, specimen thickness = 1.3–1.5 mm	5 (smoldering) 170 (flaming)	(8, 9)
Time to 90% D_m	min	National Bureau of Standards, NFPA 258, specimen thickness = 1.3–1.5 mm	18.5 (smoldering) 18.6 (flaming)	(8, 9)
Flash ignition temperature	K	ASTM D1929	843	(8, 9)
Self ignition temperature	K	ASTM D1929	893	(8, 9)
Flammability	—	UL-94	94V-O	(8, 9)

* Filler contents: 3% TiO_2; 0.5% fluorocarbon.

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Poly(amide imide)

Electrical properties of Torlon 4203L*

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric constant	—	ASTM D150		(8, 9)
		103 Hz	4.2	
		106 Hz	3.9	
Dissipation factor	—	ASTM D150		(8, 9)
		103 Hz	0.026	
		106 Hz	0.031	
Volume resistivity	ohm m	ASTM D257	2×10^{15}	(8, 9)
Surface resistivity	ohm	ASTM D257	5×10^{18}	(8, 9)
Dielectric strength	$kV\,mm^{-1}$	ASTM D149, 1 mm	23.6	(8, 9)

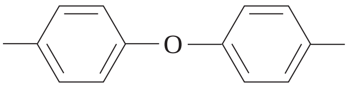
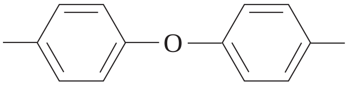
* Filler contents: 3% TiO_2; 0.5% fluorocarbon.

Other physical properties of Torlon 4203L*

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	ASTM D792	1.42	(8, 9)
Hardness, Rockwell E	—	ASTM D785	86	(8, 9)
Water absorption	%	ASTM D570	0.33	(8, 9)

* Filler contents: 3% TiO_2; 0.5% fluorocarbon.

Glass-transition temperatures (K) of poly(amide imides) derived from trimellitic anhydride (see structure above)

Ar	Conditions	Value	Reference
Torlon	—	550	(10)
	TMA in air at heating rate of $10^\circ C\,min^{-1}$	533	(11)
	Dielectric constant and dissipation factor measurements	558	(12)

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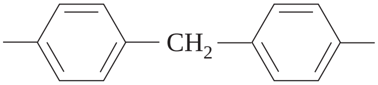
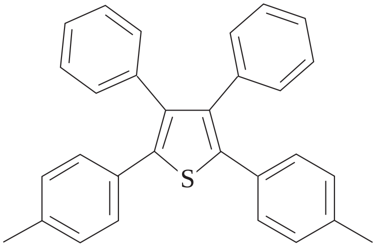
Ar	Conditions	Value	Reference
(Amoco AI-10) 	–	545	(13, 14)
	TMA in air at heating rate of $10^\circ C\,min^{-1}$	603	(2)

Glass-transition and secondary-relaxation temperatures and associated activation energy values of (Torlon)[15, 16]

Conditions	T_g (K)	E_a ($kJ\,mol^{-1}$)	T_b (K)	E_a ($kJ\,mol^{-1}$)	T_g (K)	E_a ($kJ\,mol^{-1}$)
Forced oscillation dynamic mechanical analysis at 1 Hz	549	–	338	117	204	–

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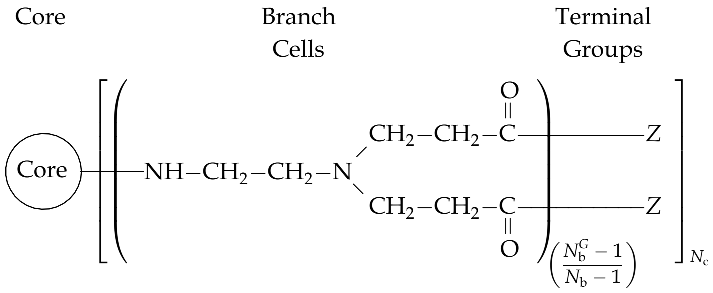
Poly(amidoamine) dendrimers

PETAR R. DVORNIC AND DONALD A. TOMALIA

ACRONYM, TRADE NAMES PAMAM dendrons and dendrimers, Starburst® dendrons and dendrimers

CLASS Dendritic polymers; dendrons; dendrimers

STRUCTURE Dendrimers are three-dimensional macromolecules consisting of three major architectural components: a core, an interior (branch cells), and terminal groups. These products are constructed from repeat units called *branch cells* (e.g., $-N(H)CH_2CH_2N[CH_2CH_2C(O)]_2$) in concentric generations (G) surrounding various initiator cores according to dendritic rules and principles, where N_c = multiplicity of core; N_b = multiplicity of branch cell; and Z = terminal groups (i.e., $-OCH_3$; $-NH-(CH_2)_2-NH_2$; $-NH-C-(CH_2-OH)_3$; or $-NH-(CH_2)_2-OH$). Core = $-[CH_2N(CH_2CH_2CO)_2]_2-$, ($N_b = 2$, $N_c = 4$), or Core = $N-[CH_2CH_2CO]_3-$, ($N_b = 2$, $N_c = 3$).



MAJOR APPLICATIONS Very precise nanoscale macromolecules (i.e., diameters between 1 and 15 nm). They are spherical, if grown from a pointlike core such as NH_3, or ellipsoidal, if grown from α, ω-alkylenediamines (e.g., $NH_2-CH_2-CH_2-NH_2$). Dendrimers are ideal macromolecular standards for use in size exclusion chromatography,[1] membrane porosity evaluation, Newtonian viscosity applications,[20] and electron microscopy.[2–4] Unique, high surface functionality (Z may range from 2, 3, or 4 to several thousand) provides nanoscopic building blocks for complex nanoconstructions based on either covalent bonding or self assembly-type processes. In the biomedical field, dendrimers have been used for drug delivery,[5–7] gene therapy,[8–11] antigen conjugates, (diagnostics)[12,13] NMR contrast agents,[14] and synthetic vaccines.[15] In the materials science area, dendrimers have been used for adhesive tie coats to glass, metal, carbon, or polymer surfaces, additives for polymer resins and composites, printing inks,[16,17] surfactants, cross-linking agents, electrically conductive nano devices,[18] flow regulators, processing aids, and chemical sensors.[19]

PROPERTIES OF SPECIAL INTEREST Unique dendrimer properties not found in traditional macromolecular architecture include: (1) a distinct parabolic intrinsic viscosity curve with a maximum as a function of molecular weight; (2) very

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monodispersed sizes and shapes (i.e., $\overline{M}_w/\overline{M}_n$ routinely below 1.1 even at high molecular weights); (3) *exo* presentation of exponentially larger numbers of surface functional groups as a function of generation (i.e., up to several thousand); (4) a *dense-shell*-type surface with a soft, spongy interior;[21] and (5) typical Newtonian-type rheology even at molecular weights exceeding 50,000 $g\,mol^{-1}$. In the PAMAM series, over 45 different surface group modifications have been reported.[22]

PREPARATIVE TECHNIQUES PAMAM dendrimers are synthesized by the divergent method starting from NH_3 ($N_c = 3$) or $H_2N{-}CH_2CH_2{-}NH_2$ (EDA) ($N_c = 4$) initiator core reagents. They are amplified by progressing through a reiterative sequence consisting of (a) a double Michael addition of methyl acrylate to a primary amino group followed by (b) amidation of the resulting carbomethoxy intermediate with a large excess of ethylenediamine (EDA). Products up to generation 10 (i.e., molecular weight of over 930,000 $g\,mol^{-1}$) have been obtained. Reactions are performed between room temperature and about 50°C in methanol. Samples are available in methanol or in water solutions. Dendrimers soluble in organic solvents (e.g., toluene or chloroform) can be readily prepared by modification of amine terminated dendrimers with hydrophobic reagents.

SUPPLIER Dendritech, Inc., 3110 Schuette Drive, Midland, Michigan 48642, USA.

Molecular properties of ethylenediamine (EDA) core PAMAM dendrimers

Generation	Number of terminal groups[a]	Molecular weight ($g\,mol^{-1}$)[a]	Hydrodynamic diameters (Å)[b]		Hydrodynamic volumes ($Å^3$)[e]	
			SEC[c]	DSV[d]	SEC	DSV
0	4	517	15.2	–	1,838	–
1	8	1,430	21.7	20.2	5,348	4,314
2	16	3,256	28.6	28.8	12,243	12,501
3	32	6,909	35.7	38.9	23,811	30,805
4	64	14,215	44.8	50.0	47,056	65,417
5	128	28,826	54.4	65.8	84,251	149,093
6	256	58,048	67.4	–	160,235	–
7	512	116,493	81	–	278,121	–
8	1,024	233,383	97	–	477,632	–
9	2,048	467,162	114	–	775,341	–
10	4,096	934,720	135	–	1,287,596	–

[a] Theoretical values.
[b] At 25°C; 0.1 molar citric acid in water; pH = 2.7.
[c] Size exclusion chromatography; relative to linear PEO standards.
[d] Dilute solution viscometry.
[e] Calculated from hydrodynamic diameters assuming ideal sphericity.

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Molecular properties of NH_3 core PAMAM dendrimers

Generation	Number of terminal groups*	Molecular weight ($g\,mol^{-1}$)*	Diameter (Å)
0	3	359	10.8
1	6	1,044	15.8
2	12	2,414	22
3	24	5,154	31
4	48	10,633	40
5	96	21,591	53
6	192	43,507	67
7	384	87,340	80
8	768	175,005	92
9	1,536	350,335	107
10	3,072	701,012	~115

*Theoretical values.

Generation dependent properties

PROPERTY	UNIT	CONDITIONS	VALUE	REFERENCE
Density (amorphous)	$g\,cm^{-3}$	Neat dendrimer in phenetol at 20°C		(23)
		EDA core; G = 0	1.178 ± 0.003	
		EDA core; G = 1	1.196 ± 0.001	
		EDA core; G = 2	1.214 ± 0.002	
		EDA core; G = 3	1.219 ± 0.007	
		EDA core; G = 4	1.224 ± 0.002	
Glass transition temperature	K	DSC; 20°C min^{-1}		(22, 23)
		EDA core; G = 0	262	
		EDA core; G = 1	270	
		EDA core; G = 2	273	
		EDA core; G = 3	284	
		EDA core; G = 4	287	
		EDA core; G = 5	287	
Steady shear viscosity	poise	75% wt. dendrimer solution in EDA; 20°C		(20)
		EDA core; G = 0; shear rate range = 0.01–170 s^{-1}	8.28	
		EDA core; G = 1; shear rate range = 0.01–20 s^{-1}	113.6	
		EDA core; G = 2; shear rate range = 0.01–3 s^{-1}	329.3	
		EDA core; G = 3; shear rate range = 0.01–2 s^{-1}	621.6	
		EDA core; G = 4; shear rate range = 0.01–1.5 s^{-1}	1,460	
		EDA core; G = 5; shear rate range = 0.01–0.75 s^{-1}	1,640	
		EDA core; G = 6; shear rate range = 0.01–0.5 s^{-1}	2,400	

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PROPERTY	UNIT	CONDITIONS	VALUE	REFERENCE
Complex viscosity	poise	Neat dendrimers at 95°C		(23)
		EDA core; G = 0; frequency range = 0.08–150 Hz	8.5	
		EDA core; G = 1; frequency range = 0.1–150 Hz	20	
		EDA core; G = 2; frequency range = 0.015–200 Hz	280	
		EDA core; G = 3; frequency range = 0.1–150 Hz	850	
		EDA core; G = 4; frequency range = 0.1–150 Hz	1,150	
		EDA core; G = 5; frequency range = 0.1–80 Hz	3,000	
Electrical conductivity	$S\,cm^{-1}$	Diimide anion radical modified EDA core, generation 3 PAMAM dendrimer. Film; 4 point measurement; 90% relative humidity	11	(18)

Generation independent properties[23]

PROPERTY	UNIT	CONDITIONS	VALUE
Solvents		Water; methanol; DMF,DMSO	
Nonsolvents		Most aliphatic and aromatic solvents, THF, chloroform	
Thermal stability	K	Neat dendrimer in nitrogen; dynamic TGA; 20°C min^{-1}	453
		Neat dendrimer in nitrogen; isothermal TGA for 16 h; weight loss less than 1%	443
Thermo-oxidative stabiltiy	K	Neat dendrimer in air; dynamic TGA; 20°C min^{-1}	433
		Neat dendrimer in air; isothermal TGA for 16 h; weight loss less than 1%	373

Practical matters

PROPERTY	CONDITIONS	VALUE
Availability	Gold standards: low defect levels, biomedical applications	Units: 100 mg; 500 mg; g
	Technical grade: higher defect levels, reduced regularity, materials applications	Units: kg
Suppliers	Gold standards (mg); technical grade (kg)	Dendritech, Inc., 3110 Scheutte Drive, Midland, Michigan 48642, USA
	Primary amine, sodium carboxylate, and certain hydroxyl surface groups are available	Aldrich Chemical Company, Inc., 1001 West St. Paul Avenue, Milwaukee, Wisconsin 53233, USA

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PROPERTY	VALUE
Significant patents for composition of matter	U.S. Patent 4,507,466 (1985) U.S. Patent 4,558,120 (1985) U.S. Patent 4,568,737 (1986) U.S. Patent 4,587,329 (1986) U.S. Patent 4,631,337 (1986) U.S. Patent 4,694,064 (1986) U.S. Patent 4,857,599 (1989)

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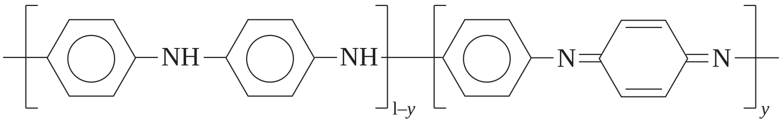
Polyaniline

STEPHEN S. HARDAKER AND RICHARD V. GREGORY

ACRONYM, ALTERNATIVE NAMES, TRADE NAMES PANI, emeraldine, leucoemeraldine, pernigraniline, Ormecron (Zipperling Kessler and Co.), Zypan (Du Pont)

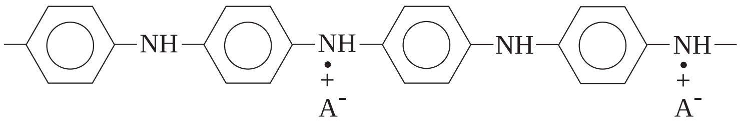
CLASS Conjugated and other unsaturated polymers; electrically conductive polymers

STRUCTURE Polyaniline base of variable oxidation state



$y = 0$: Leucoemeraldine base (LEB)
$y = 0.5$: Emeraldine base (EB)
$y = 1$: Pernigraniline base (PNB)

Emeraldine salt (ES)



MAJOR APPLICATIONS Polyaniline is finding widespread use in novel organic electronic applications such as: light emitting diodes (LED), electroluminescense, metallic corrosion resistance, organic rechargeable batteries, biological and environmental sensors, composite structures, textile structures for specialized applications or static dissipation, membrane gas-phase separation, actuators, EMI shielding, organic semiconductor devices for circuit applications, blends with insulative host polymers to impart a slight electrical conductivity, bioelectronic medical devices, and a variety of other applications where tunable conductivity in an organic polymer is desirable.

PROPERTIES OF SPECIAL INTEREST Electrical conductivity in the range of 10^{-8} to $400\,S\,cm^{-1}$. This conductivity will increase as better processing methods are developed reducing structural defects. The conductivity can be tuned to specific end uses for a variety of applications. Polyaniline is reasonably stable under ambient conditions and, with the proper selection of dopants, retains its conductivity over long periods of time (i.e., five years and longer). Polyaniline easily switches from the conductive form (emeraldine salt) to the insulative form (emeraldine base) as a function of pH. Under acidic conditions the polymer acid dopes and becomes conductive. When exposed to higher pH levels the polymer switches to the insulative form. This facile switching can be cycled many times.

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Polyaniline

Unit cell dimensions[1]

Form	*a* (Å)	*b* (Å)	*c* (Å)	Lattice	Comments
EB-II	7.80	5.75	10.05	Orthorhombic	NMP-cast, stretched film
	7.65	5.75	10.20	Orthorhombic	THF/NMP-extracted powder
	7.65	5.65	10.40	Orthorhombic	Powder from THF-extracted solution
ES-II	7.1	7.9	10.4	Orthorhombic	NMP-cast, stretched film, HCl dopant
	7.0	8.6	10.4	Orthorhombic	THF/NMP-extracted powder, HCl dopant
ES-I	4.3	5.9	9.6	Pseudoorthorhombic	As synthesized, HCl dopant

Solubility parameters of polyaniline and several solvents

Compound	δ ($MPa^{1/2}$)	δ_d ($MPa^{1/2}$)	δ_p($MPa^{1/2}$)	δ_h($MPa^{1/2}$)	Comment	Reference
Emeraldine base	22.2	17.4	8.1	10.7	Empirical	(2)
Emeraldine salt	23.6	17	8.9	13.7	Empirical	(2)
Leucoemeraldine base	23–25	21.1	5.6	7.3	Empirical	(2)
1-Methyl-2-pyrrolidinone (NMP)	23.7	16.5	10.4	13.5	Calculated	(2)
N,N′-dimethyl propylene urea (DMPU)	22.3	16.4	11.3	10.0	Calculated	(3)
m-Cresol	22.7	18.7	4.8	13.5	Calculated	(2)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Permeability	m^3(STP) m s^{-1} m^{-2} Pa^{-1}	Gas		(4)
		H_2	3,580	
		CO_2	586	
		O_2	123	
		N_2	13.4	
		CH_4	3.04	
Huggins parameter: k'	—	Form/Solvent		(5)
		EB/NMP	0.384	
		EB/DMPU	0.371	
Storage modulus	MPa	EB form; EB film cast from NMP; DMTA, 1 Hz, 25°C	2,000	(6)
		ES-HCl form; EB film cast from NMP then doped with HCl; DMTA, 1 Hz, 25°C	2,300	
Loss modulus	MPa	EB form; EB film cast from NMP; DMTA, 1 Hz, 25°C	256	(6)
		ES-HCl form; EB film cast from NMP then doped with HCl; DMTA, 1 Hz, 25°C	218	

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Mechanical properties of polyaniline fibers

Fiber process[a]	Base			Dopant	Doped			Conductivity ($S\,cm^{-1}$)	Reference
	Tenacity (gpd)[b]	Modulus (gpd)[b]	Elongation (%)		Tenacity (gpd)[b]	Modulus (gpd[b])	Elongation (%)		
PANI-CSA/*m*-cresol[c]	n/a	n/a	n/a	CSA	0.2	7.3	8.4	203	(7)
PANI-EB/H_2SO_4	n/a	n/a	n/a	H_2SO_4	1.8	39.3	25.4	6.3	(7)
PANI-EB/NMP[d] drawn	3.9	–	–	HCl	1.4	–	–	160	(8)
PANI-EB/DMPU as-spun	0.2–0.6	27	7	CH_3SO_3H	<0.2	–	–	10–32	(9)
PANI-EB/DMPU 4× drawn	2.4	56	13	CH_3SO_3H	<1.0	–	–	350	(9)
PANI-LEB/DMPU as-spun	1.1	57	51	CH_3SO_3H	0.8	–	–	15	(10)
PANI-LEB/DMPU 2× drawn	3.6	89	15	HCl	1.9	–	–	140	(10)

[a] Fiber process is designated as: polyaniline form/solvent, post process.
[b] gpd ≡ g $denier^{-1}$. Denier is a linear density: 1 denier = 1 g $(9{,}000\,m)^{-1}$.
[c] Mixture of emeraldine base and (±)-camphor sulfonic acid dissolved in *m*-cresol.
[d] Solution also contained a gel inhibitor.

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Room temperature conductivity	$S\,cm^{-1}$	CSA dopant; film cast from *m*-cresol; PANI-CSA complex formed in solution	400		(11)
		CH_3SO_3H dopant; fiber spun in EB form from DMPU and 4× drawn then doped	350		(9)
		CSA dopant; as-spun fiber from *m*-cresol; EB and CSA mixed as powder	203		(7)
		CSA dopant; film cast from 30/70 chloroform/*m*-cresol; EB and CSA mixed as powder	70		(11)
		CH_3SO_3H/acetic acid dopant; film cast from EB/DMPU then doped	60		(5)
		HCl dopant; film cast from EB/NMP and 4× drawn then doped	24		(12)
		I_2 dopant; spin-coated from LEB/DMPU then doped	11.4		(13)
		H_2SO_4 dopant	6.31		(14)
Apparent bandgap (absorption)	eV	Polyaniline form	Onset	Peak	(11)
		LEB	3.2	3.6	
		EB	1.6 (3.0)	2.0 (3.8)	
		PNB	1.8	2.3	
Melting temperature	K	LEB film and fiber from DMPU; DSC, 20°C min^{-1}, N_2	658		(15)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature	K	LEB fiber spun from DMPU; DSC, 5°C min^{-1}, N_2	474	(16)
		EB film cast from NMP; DMTA, 5°C min^{-1}, 1 Hz	493	(6)
Sub-T_g transition temperature	K	EB film cast from NMP; DMTA, 3°C min^{-1}, 1 Hz; assigned to phenyl ring twisting	193	(17)
Thermal stability	K	Cross-linking reaction; EB film cast from NMP; DMTA, 3°C min^{-1}, 1 Hz	453	(17)
		Decomposition (LEB) reaction; LEB spin coated film from DMPU; TGA, 20°C min^{-1}, N_2	780	(15)
		Decomposition (EB) reaction; EB film cast from NMP; TGA, 20°C min^{-1}, N_2	673	(6)
Index of refraction n	–	EB spin-coated from DMPU, average, 1,550 nm	1.85	(18)
Zero-T dielectric constant $\varepsilon_{mw}(T \to 0)$	–	PANI-CSA cast from chloroform	~30	(11)
Dielectric constant ε_{mw}	–	PANI-CSA cast from *m*-cresol, 300 K, 6.5 GHz	-4.5×10^{-4}	(11)
Plasma frequency ω_p	eV	PANI-CSA cast from *m*-cresol, 300 K	0.016	(11)
Dielectric relaxation time τ	s	PANI-CSA cast from *m*-cresol, 300 K	1.1×10^{-11}	(11)
Electroluminescence emission peak	nm	Porous Si/PANI-CSA(*m*-cresol), 0.5 A cm^{-2} current density	800	(19)

Surface energies[20]

Form	Surface Energy			Comments
	γ (erg cm^{-2})	γ^d (erg cm^{-2})	γ^p (erg cm^{-2})	
EB	44.6	36.9	7.7	NMP cast film
PANI-HCl	63.5	38.7	24.8	NMP cast EB; doped with HCl (pH = 0)

Electrochemical potentials of redox processes in polyaniline

Redox Couple	Potential* (V)	Conditions	Reference
Leucoemeraldine/emeraldine	0.15	vs. Cu/CuF_2 in $NH_4F + 2.3HF$	(21)
Emeraldine/pernigraniline	0.80	vs. Cu/CuF_2 in $NH_4F + 2.3HF$	(21)
Leucoemeraldine/emeraldine	0.115	vs. SCE in 1.0 M HCl	(22)
Emeraldine/pernigraniline	0.755	vs. SCE in 1.0 M HCl	(22)

* Reported potentials are average of oxidation and reduction potentials for a given redox couple.

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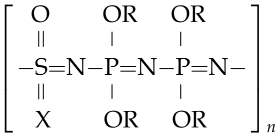
Poly(aryloxy)thionylphosphazenes

JOSEPH H. MAGILL

ACRONYMS PATP, PTP

CLASS Polyphosphazenes; poly(thionylphosphazenes)

STRUCTURE $-[(NSOX)(NP(OAr_2)_2)]_n-$ (X = Cl in this context)



MAJOR APPLICATIONS Experimental specimens have considerable potential interest. There are ongoing evaluations and development of these new types of noncrystalline polymers.[1–6]

PROPERTIES OF SPECIAL INTEREST Film-forming elastomers, potential oxygen sensors for biomedical and aerospace are among this class of poly(thionylphosphazenes) depending upon substituents present.[3,4,6]

SYNTHESIS TECHNIQUES AND TYPES OF STRUCTURES Thermal ring-opening polymerization of cyclic thiophosphazene—comprehensive reviews on the chemistry of halogen side-group replacement reactions in cycloheterophosphazenes have been published by van de Grampel[2]—to produce a linear polymer intermediate.[2] Upon reaction of this halo side group intermediate—these elastomeric materials are hydrolytically sensitive as are other halogenated polymer intermediates—with organic nucleophiles poly(thiophosphazenes) are produced, whose properties depend on the nature of the substituents. A wide variety of material properties are anticipated following these procedures. To date only amorphous polymers have been synthesized and characterized by conventional analytical methods.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Chemical structure and properties	–	Depends upon substituents	Variable	(5, 6)
Molecular mass (of repeat unit)	$g\,mol^{-1}$	–	569.64	–
Typical molecular weight	$g\,mol^{-1}$	GPC	$M_w = 1.4 \times 10^5$ $M_n = 5.1 \times 10^4$	–
Typical polydispersity M_w/M_n	–	–	<3	–
Solvents	Generally THF, toluene, chlorinated hydrocarbons such as CH_2Cl_2, etc.			(7)
Nonsolvents	Nonpolar (hexanes) or highly polar H-bonded liquids such as H_2O or MeOH			(7)

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Spectroscopic properties

PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
UV-visible spectrum	Nm	Unresolved peaks	252; 272	(6)
IR-spectrum	cm^{-1}	Thin films cast on KBr disks		–
		S=O	1,307	
		P=N	1,203	
		C–O	1,165	
		S=O	1,148	
		P–O	967	
NMR-spectrum (solution)	ppm	^{1}H in $CDCl_3$	7.1 (m)	(6)
		^{31}P in CHCl2	−20.9	
		^{31}C in CDCl3		
		o-Ph	121.3	
		m-Ph′	126.9	
		p-Ph′	127.2	
		o-Ph′	128.0	
		m-Ph′	128.8	
		p-Ph	138.1	
		ipso Ph′	139.9	
		ipso Ph′	149.9	
		ipso Ph, all s	149.9	

* Ph denotes the phenyl ring closest to the polymer backbone; Ph′ refers to the ring furthest away.[6] *Ab initio* molecular orbital calculations depicting conformational parameters are compiled in reference (4).

Transition temperatures

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature*	K	DSC method (10° min^{-1} heating rate)	328	(6)
Mesophase transition	–	DSC method (10° min^{-1} heating rate)	None reported	–
Melting temperature	–	DSC method (10° min^{-1} heating rate)	None reported	–

* Values are reported for various poly(thiophosphazenes) ranging from 217 to 330 K, depending on the side groups and molecular weight.[4,6,8]

Solution properties

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Solvents	–	–	THF, CH_2Cl_2, dioxane	(7)
Theta temperature Θ	K	THF solution, $M_w = 6.4 \times 10^{4}$*	295	(6)
Hydrodynamic Stokes	Å	THF, 295 K, $M_w = 6.4 \times 10^{4}$	59 (radius, R_h, eff.)	(6)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Diffusion coefficient	$cm_2\,s^{-1}$	THF, 295 K, $M_w = 6.4 \times 10^4$	7.75×10^{-7}	—
Second virial coefficient	$mol\,cm^3\,g^{-2}$	THF, 295 K, $M_w = 6.4 \times 10^4$	~0.0	—
Refractive index increment dn/dc	$ml\,g^{-1}$	THF, 295 K, $M_w = 6.4 \times 10^4$	0.208	—

* There is an apparent discrepancy in molecular weights measured by GPC and low-angle laser light scattering (LALLS) techniques.[6] GPC overestimates it by about 30% unless corrections are made to coil size between the phosphazene and the polystyrene calibrant.

Stabilities

CONDITIONS	VALUE
In air (years)	Stable
In hot solution, NaOH or Na aryloxide	Rapidly decomposes by nucleophilic attack at the S in backbone

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Poly(*p*-benzamide)

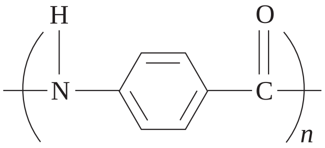
GURU SANKAR RAJAN

ACRONYMS PBA, PPBA

CLASS Aromatic polyamides

REGISTRY PBA (SRU) 24991-08-0; PBA (homopolymer) 25136-77-0.

STRUCTURE[1–6]

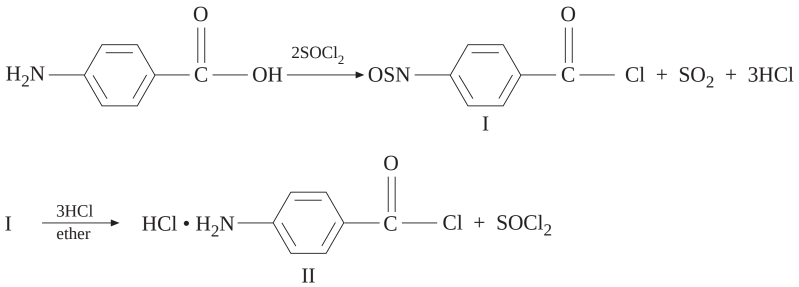


GENERAL INFORMATION PBA is the first nonpeptide, synthetic condensation polymer (AB type) reported to form a liquid-crystalline solution.[1] PBA is obtained by the low-temperature solution polymerization as described by Kwolek.[1] Other methods include those of Memeger,[5] Russo,[7] or Preston.[8,9] PBA forms liquid-crystalline solutions because of an inherently extended rigid chain structure produced by a combination of a para-linked benzene ring and partial double-bond character of the carbon-nitrogen bond in predominantly *trans* amide linkages.[1] The molecular conformation is TCTC, where the internal rotation angles about the N–C bond of the amide group and about the virtual bond of N–phenyl–C are T (*trans*) and C (*cis*) conformations, respectively.[10] The chain of all amide groups is in the ''head-to-tail'' order for PBA.[11]

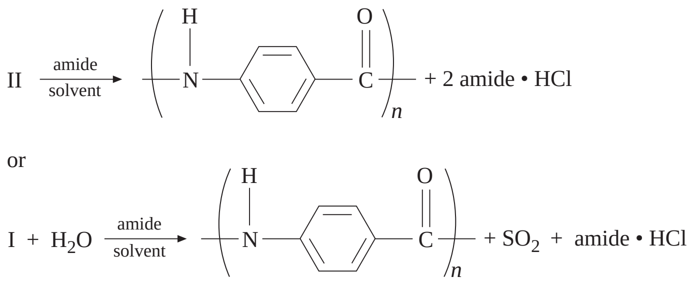
MAJOR APPLICATIONS The dopes of PBA can be utilized for the preparation of films, filaments, fibrids, and coatings. Wet-extruded, tough, clear, flexible films can be applied to substrates like glass, ceramics, metals, concrete, and polymeric materials.[12] The high-temperature resistance of the polyaramids make them suitable for asbestos replacement in heat-resistant work wear. The service life is longer for asbestos and the wearing comfort is greater. PBA has been superseded by poly(*p*-phenylene terephthalamide).[13]

Synthesis

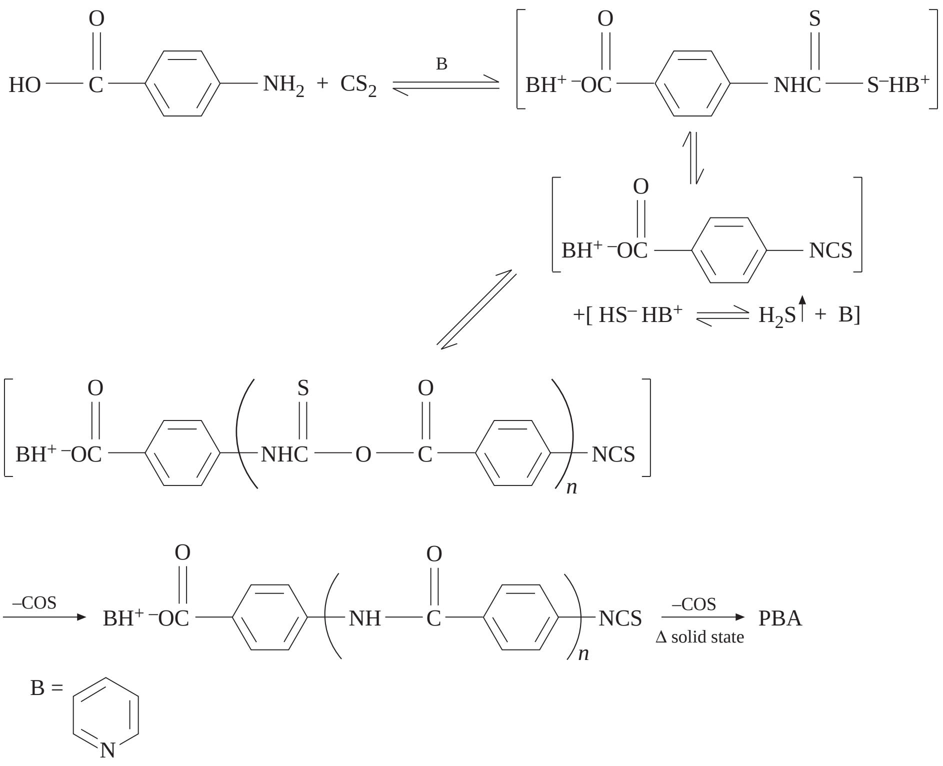
Scheme 1 from reference (1)



Scheme 1 from reference (1)



Scheme 2 from reference (5)



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Intrinsic viscosities, molecular weights (M_w and M_n), and M_w/M_n[14]

$[\eta]^*$ ($dl\,g^{-1}$)	M_w ($g\,mol^{-1}$)	M_n ($g\,mol^{-1}$)	M_w/M_n
0.46	5,300*	2,700	2.0
0.88	6,800*	4,400	1.5
1.21	7,250*	4,250	1.7
1.15	8,700*	–	–
1.62	10,400*	5,750	1.8
2.08	11,700*	6,760	1.7
2.10	12,400*	–	–
2.20	13,800*	–	–
2.43	14,200*	–	–
5.20	26,000†	–	–
9.00	51,000†	–	–
12.5	64,400*	–	–

*In concentrated sulfuric acid.
†In chlorosulfonic acid, 0.1 N $LiClSO_3$.

Mark-Houwink parameters: *K* and *a*[14–16]

Range	K ($dl\,g^{-1}$)	Author	a
<12,000*	1.9×10^{-7}	Schaefgen, <12,000*	1.70
>12,000*	7.8×10^{-5}	Schaefgen, >12,000*	1.08
$3,100 \leq M_w \leq 13,000$*	2.14×10^{-5}	Arpin*	1.20
$5,300 \leq M_w \leq 51,000$*	1.67×10^{-5}	Chu†	1.46
$7,140 \leq M_w \leq 23,000$*	2.69×10^{-5}	Papkov†	1.85

*In H_2SO_4.
†In dimethyl acetamide +3% LiCl.

Average molecular weight and MWD using different methods of data analysis[11]

Method	Sample	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$M_z \times 10^{-4}$	M_w/M_n	M_z/M_w
CONTIN	4	2.63	4.77	11.8	1.82	2.47
	5	1.81	3.00	6.69	1.66	2.23
MSVD	4	2.30	3.84	10.8	1.67	2.80
	5	2.20	3.28	8.67	1.49	2.64

Observed band frequencies for the *cis-trans* conformation by infrared spectroscopy[17]

Intensity	Frequency (cm^{-1})
Very strong	1507, 1319, and 1238
Strong	3346, 1662, 1605, 1593, 1527, 1410, 1402, 1272, 1186, and 847
Medium strong	1091
Medium	1127, 1019, 807, and 764
Weak	3062, 3036, 701, 691, 631, 539, and 486
Very weak	972, 950, and 601

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Relaxation times of selected ^{13}C resonances*[18]

T_1 (ms)† and T_2 (ms)† at 126 ppm (protonated aromatic, isotropic site) are 130 ± 10 and 1.20 ± 0.30; at 131 ppm (protonated aromatic, isotropic site) are 140 ± 10 and 1.25 ± 0.50; at 154 ppm (protonated aromatic, nematic site) are 120 ± 20 and 0.90 ± 0.20; at 159 ppm (protonated aromatic, nematic site) are 110 ± 20 and 1.15 ± 0.40; at 173 ppm (carbonyl, isotropic site) are 470 ± 70 and 1.90 ± 0.70; and at 205 ppm (carbonyl, nematic site) are 450 ± 100 and 1.60 ± 1.00, respectively.

*Under conditions of nematic/isotropic coexistence (inversion-recovery and spin-echo data fits on 12.4% w/w PBA/H_2SO_4 solutions at 45°C).
†Error margins denote the standard deviations of the fits.

Shift of fluorescence peak wavelength*[19]

λ_{ex} (nm) at 380, 390, 400, 410, 420, and 465.
Peak λ_{ex} (nm) at 431, 431, 460, 478, 496, and 513.

*For a 0.1% solution of PBA in H_2SO_4.

Standard values for bond lengths (Å) and bond angles (degrees)[10]

Bond lengths for C1=O, C1–C7, C1–N, N–H1, C–C (phenyl), and C–H (phenyl) are 1.24, 1.50, 1.35, 0.96, 1.395, and 1.084, respectively.
Bond angles for O′–C1′–C7, C7–C1′–N′, O–C1–N, C1–N–H1, C1–N–C2, and H1–N–C2 are 120.9, 116.3, 122.8, 117.9, 124.5, and 117.6, respectively.

Average thermal expansion coefficients between 300 and 500 K[20,21]

Expansion cefficients (10^{-5} K^{-1})	Calculated	Experimental
α_1	7.7	7.0
α_2	4.6	4.1
α_3	−0.84	−0.77

Solvents and nonsolvents[12,22]

Solvents	Tetramethylurea (TMU), N,N-dimethylacetamide (DMAc), N-methylpyrrolidone (NMP), N,N-dimethyl ethylene urea, N-acetylpyrrolidone, N,N-diethylacetamide, N-ethylpyrrolidone, N,N-dimethylpropionamide, N,N-dimethylbutyramide, and N,N-dimethylisobutyramide. (Li or Ca chloride can increase the solubility of sparingly soluble rodlike aromatic polyamides such as PBA in DMAc, TMU, and NMP)
Nonsolvents	Water bath (65–90°C), ethylene gylcol, glycerol, mixtures of TMU and water, mixtures of alcohol and water, and aqueous salt baths (preferably maintained at 40–45°C or above)

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Values of the two phases of a solution of PBA in TMU-LiCl[1]

Property	Units	Isotropic phase	Optically anisotropic phase
Proportion	% by volume	31	69
Density	$g\,cm^{-3}$	1.0598	1.0664
LiCl content	$g\,cm^{-3}$	0.085	0.082
Polymer content	$g\,cm^{-3}$	0.105	0.121
Polymer η_{inh}	$dl\,g^{-1}$	0.59	0.88
Bulk viscosity	cP	~6,000	3,000

Static and dynamic properties of PBA in DMAc + 3% $(g\,cm^{-3})$ LiCl[11]

Sample	$M_w \times 10^{-4}$	Second virial coefficient $A_2 \times 10^{-3}$ $(cm^3\,mol\,g^{-2})$	Radius of gyration R_g (nm)	Persistence length q (Å)	Anisotropy δ
1	5.17	1.63	32	750 ± 30	0.40
2	5.52	0.31	36	750 ± 30	0.40
3	22.9	0.59	90	—	(0.22)
4	4.41	—	—	750 ± 30	0.41
5	2.88	—	—	750 ± 30	0.51

Persistence lengths and Kuhn segments[23–26]

Method	Kuhn segment (Å)	q (Å)	Method	Kuhn segment (Å)	q (Å)
Sedimentation (in DMAc + LiCl)	380–390	190–195	Flow bifringence (in H_4SO_4)	2,100	1,050
Light scattering (in H_2SO_4)	—	400	—	1,960	980
Viscosity (in H_2SO_4)	—	180–240	—	1,000	500

Constants* for the clearing temperatures[27]

M_w	A	α
10,000	41 (6)	0.92 (0.06)

*A and α are from least-squares fits of the clearing temperature (T_{ni}) versus concentration (c) measurements to a relation of the form $T_{ni} = Ac^{\alpha}$. The standard deviations of A and α are shown in parentheses.

Thermal properties[28–30]

Property	Units	Value
Glass transition temperature*	K	>503
Crystal transformation temperature	K	487 (modification I to II)
Crystal-nematic transition temperature†	K	748 (II)
		817 (III)

*The DSC thermogram of the PBA crystalline solvate exhibits two broad endotherms in the 120–230°C temperature range, which disappears when the sample anneals above 230°C, but a different crystal form appears.

†By heating II above 475°C and cooling, or by washing with water, or by washing I with water and annealing, III can be obtained.

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Crystallographic data[10,28,31]

Parameters	Units	Reference (28)	Reference (31)	Reference (10)
Crystal system	—	Orthorhombic	—	—
Space group	—	P212121-D24	—	P212121-D24
Lattice constants	Å			
a		7.71	8.06	7.75
b		5.14	5.13	5.30
c (fiber axis)		12.8	12.96	12.87
Density	$g\ cm^{-3}$			
Observed		1.48	1.48	1.48
Calculated		1.54	1.48	1.50
Number of chains in a unit cell	—	2	1	2

Isothermal liquid crystallization data[32]

Property	Units	PBA/H_2SO_4 system			
Liquid crystallization temperature	K	318	323	328	333
Avrami exponent n	—	1.35	1.20	1.15	0.95
Half-time for the liquid crystallization $t^{1/2}$	s	8.8	11.4	16.4	22.7

Effect of anisotropy on fiber properties ($\eta_{inh} = 2.1$, in H_2SO_4)[1]

Anisotropic phase in spin dope	Spin dope*		As-extruded filaments			
	η (cP)	Wt% of polymer	Tenacity ($N\ tex^{-1}$)	Elongation (%)	Initial modulus ($N\ tex^{-1}$)	Orientation angle (degrees)
None	14,000	4.6	0.39	10.9	16.1	33
Small amount	5,600	5.8	0.75	9.7	29.1	20
Larger amount	1,800	6.7	0.86	8.3	37.4	16

*Spin dope = 13% in tetramethylurea-lithium chloride (6.54%).

Mechanical properties of undrawn fiber by dry spinning ($\eta_{inh} = 1.48$, in H_2SO_4)[1]

Spin stretch factor*	Tex per filament	Tenacity ($N\ tex^{-1}$)	Elongation (%)	Initial modulus ($N\ tex^{-1}$)	Orientation angle (degrees)
Free fall	0.67	0.28	3.7	12.4	39
1.90	0.68	0.33	2.7	20.7	37
2.42	0.53	0.37	3.4	19.4	38
2.56	0.56	0.46	3.3	24.7	26
3.83	0.34	0.61	2.9	34.4	22
5.11	0.26	0.76	3.0	41.5	22
6.39	0.21	0.71	2.8	38.0	19

*Spin dope = 13% in tetramethylurea-lithium chloride (6.54%).

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Effect of spinning method on fiber properties[33, 34]

η_{inh} ($dl\,g^{-1}$)[a]	Spun from[b]	Spinning method[c]	Tex per filament	Tenacity ($N\,tex^{-1}$)	Elongation to break (%)	Initial modulus ($N\,tex^{-1}$)
1.67	O(-)	D	–	0.72	3.1	44.9
2.36	O(A)	W	0.54[d]	0.64	8.1	25.0
Same dope	O(I)	W	2.53[e]	0.11	9.0	5.6
3.7	A(A)	DJ-W	0.11	1.7	4.0	50.3

[a]In H_2SO_4.
[b]O = organic solvent; A = acid (H_2SO_4); (I) = isotropic dope; (A) = anisotropic dope.
[c]D = dry-spun; W = wet-spun; DJ-W = dry-jet–wet-spun.
[d]Spun from anisotropic layer of dope.
[e]Spun from isotropic layer of dope.

Tensile properties before and after annealing[13]

	Units	Dry spinning*	Annealing†
Tensile modulus	MPa	65,000	137,000
Tensile strength	MPa	1,050	2,200
Elongation to break	%	3.1	1.9

*Spin stretch factor of 3.2.
†Brief annealing for a few seconds at 525°C under nitrogen.

Literature available

Poly(*p*-benzamide)	Reference
Synthesis, anisotropic solutions, and fibers	(1–9, 12)
Crystal structure	(4, 6, 10, 11, 45)
Phase diagrams, composition and fractionation	(4, 6, 43, 47, 48, 50–52, 54)
Static and dynamic properties	(11)
Mechanical properties	(12, 13, 33, 34)
Optical properties	(55, 56)
Viscosity-molecular weight relationships	(14–16, 57)
IR, Jacobian and force constants, NMR, chemical shift tensor parameters, fluorscence spectra	(17–19, 23)
Thermal expansion and isothermal elastic stiffness constants	(20, 21)
Solubility, persistence length, effect of solvent on the structure and property	(1, 2, 5, 12, 22–26, 58)
Surface tension	(59)
Diffusion and sedimentation	(60)
Thermal transition, thermal behavior, clearing temperatures	(27–30)
Magnetic field orientation	(28)
Characterization and conformation	(23)
Vapor permeation	(49)
Kinetics of liquid crystallization	(32)
Dynamic birefringence, rigidity	(35, 45, 53)
Patents	(12, 36–41)
Thermomechanical and ultrasonic properties	(44)
Moments of end-to-end vectors, order parameter	(42, 46)
Molecular simulation	(31)

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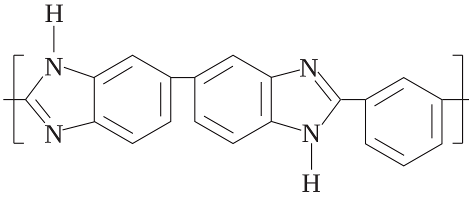
Poly(benzimidazole)

WILLIAM J. WELSH

ACRONYMS, ALTERNATIVE NAME PBI, PBZI, poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole]

CLASS Rigid-rod polymers

STRUCTURE



MAJOR APPLICATIONS Fire-resistant material, replacement for asbestos, thermal-protective clothing, ion-exchange resins, microporous absorbent beads, membrane applications.

PROPERTIES OF SPECIAL INTEREST High-temperature stability, nonflammability, unusual resistance to organic solvents, excellent mechanical properties, interesting electrical and nonlinear optical properties.

SYNTHESIS Condensation polymerization of 3,3′,4,4′-tetraaminobiphenyl (TAB) and diphenyl isophthalate (DPIP) in poly(phosphoric) acid,[1] or in a hot molten nonsolvent such as sulfolane or diphenyl sulfone.[2]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	Fiber, stabilized	1.43	(3)
		Fiber, unstabilized	1.39	
		Fiber-grade film		
		Untreated	1.2	
		Annealed	1.3	
		Plasticized	1.4	
Young's modulus	N/tex	Fiber, stabilized	39.6	(3)
		Fiber, unstabilized	79.2	
	MPa	Fiber-grade film		
		Untreated	2,750	
		Annealed	3,790	
		Plasticized	2,270	
		High MW film		
		Untreated	3,170	
		Plasticized	2,820	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength (tenacity)	N/tex	Fiber, stabilized	2.3	(3)
		Fiber, unstabilized	2.3	
	MPa	Fiber-grade film		
		Untreated	117	
		Annealed	186	
		Plasticized	103	
		High MW film		
		Untreated	96	
		Plasticized	96	
Elongation at break	%	Fiber	30	(3)
		Fiber-grade film		
		Untreated	14	
		Annealed	24	
		Plasticized	20	
Glass transition temperature T_g	K	–	~700	(3)
		After annealing	773	
Thermal decomposition onset	K	–	~873	(3)
Flame-test shrinkage	%	Fiber, stabilized	6	(3)
		Fiber, unstabilized	50	
Moisture content	%	Fiber, stabilized, 21°C, 65% relative humidity	15	(3)
		Fiber-grade film		
		Untreated	10	
		Annealed	5	
		Plasticized	12	
		High MW film		
		Untreated	10	
		Plasticized	12	
Surface resistivity	ohm sq^{-1}	Film	10^{11}	(3)
Volume resistivity	ohm cm	Film	10^{13}	(3)
Dielectric constant	–	Film, at 100 Hz		(3)
		25°C	5.4	
		250°C	3.7	
Dielectric strength	$V m^{-1}$	Film, at 100 Hz		(3)
		25°C	3,900	
		250°C	2,500	
Dissipation factor	–	Film, at 100 Hz		(3)
		25°C	0.013	
		250°C	0.021	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Bulk protonic conductivity	$ohm^{-1}\ cm^{-1}$	Film, at 100% relative humidity	8×10^{-5}	(3)
Characteristic peaks	cm^{-1}	FTIR, dry polymer film		(4)
		Aromatic C–H stretch	3,150	
		Imidazole free N–H stretch	3,420	
		FTIR, wet polymer		
		Aromatic C–H stretch	3,150	
		Imidazole free N-H stretch	3,420	
		Water O–H stretch	3,620	

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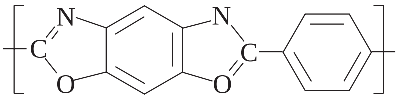
Poly(benzobisoxazole)

WILLIAM J. WELSH

ACRONYM, ALTERNATIVE NAMES PBO, poly(*p*-phenylene-2,6-benzoxazolediyl), poly[(benzo[1,2-d:5,4-d′]bisoxazole-2,6-diyl)-1,4-phenylene]

CLASS Rigid-rod polymers

STRUCTURE



MAJOR APPLICATIONS High-performance films, fibers, and coatings.

SYNTHESIS Polycondensation of a terephthalic acid with 4,6-diamino-1,3-benzenediol dihydrochloride in poly(phosphoric acid). Processing is primarily limited to variations of wet extrusion.[1,2]

PROPERTIES OF SPECIAL INTEREST High-temperature resistance, unusual resistance to organic solvents, excellent mechanical properties, interesting electrical and nonlinear optical properties.

SOLUBILITY (a) Protonic sulfonic acids RSO_3H, where R = $-OH$, $-CH_3$, $-Cl$, $-CF_3$, $-C_6H_5$, etc., polyphosphoric acid (PPA), *m*-cresol/dichloroacetic acid (70/30), dichloroacetic acid/MSA (90/10).[1] (b) Aprotic organic solvents (e.g., nitroalkanes) containing metal halide Lewis acids (e.g., $AlCl_3$, GaC_3, $FeCl_3$)—up to 7.5% polymer.[3]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	As-spun fiber	1.50	(4)
		Fiber	1.58	(5)
		X-ray diffraction data	1.50	(6)

Unit cell dimensions

Lattice	Monomers per unit cell	Cell dimensions (Å)			Cell angles (degrees)			Reference
		a	*b*	*c* (chain axis)	α	β	γ	
Monoclinic	2	11.20	3.540	12.050	90	90	101.3	(6)
Monoclinic	1	5.65	3.58	11.74	90	90	102.5	(7)
Monoclinic	1	5.598	3.540	12.05	90	90	102.5	(8)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Young's (tensile) modulus	g denier^{-1}	Fiber, as-spun	502	(9)
		Fiber, heat-treated	711	(9)
	GPa	Ribbons	7.6	(9)
		Along fiber or draw direction)	85	(10)
		Perpendicular to fiber or draw direction)	6.5	(10)
		Fiber, heat treated (value depends on MW)	221–304	(4)
		Fiber, as-spun	144	(11)
		Heat treated (600°C)	250	(11)
		Geat-treated (650°C)	262	(11)
		Fiber	200–360	(5)
		Fiber	370	(7)
		Fiber	317, 365	(12)
		Fiber, as-spun	166	(13)
		Heat-treated (600°C)	318	(13)
		Heat-treated (665°C)	290	(13)
		Fiber, as-spun	144 $\pm$ 23	(14)
		Heat-treated (600°C)	250 $\pm$ 20	(14)
		Heat-treated (650°C)	262 $\pm$ 25	(14)
X-ray modulus	—	Fiber, as-spun	387	(13)
		Heat-treated (600°C)	477	(13)
		Heat-treated (665°C)	433	(13)
Compressive modulus	GPa	Fiber	240	(15)
Tensile strength	g denier^{-1}	Fiber , as-spun	4.2	(2)
		Fiber, heat-treated	4.8	(2)
	GPa	Ribbon	0.103	(3)
		Fiber	4.9, 5.8	(12)
		Fiber, as-spun	2.31	(4)
		Fiber, as spun	4.6	(11)
		Heat-treated (600°C)	5.1	(11)
		Heat-treated (650°C)	3.4	(11)
		Fiber	3.0–5.7	(5)
		Fiber	3.6	(7)
		Fiber, heat-treated (value depends on MW)	2.2–4.7	(4)
		Fiber, as-spun	4.6	(13)
		Heat-treated (600°C)	4.9	(13)
		Heat-treated (665°C)	3.0	(13)
		Fiber, as-spun	4.6 $\pm$ 0.5	(14)
		Heat-treated (600°C)	5.1 $\pm$ 0.6	(14)
		Heat-treated (650°C)	3.4 $\pm$ 0.5	(14)
Elongation at break	%	Fiber, as-spun	1.4	(2)
		Fiber, heat-treated	0.7	(2)
		Ribbon	0.8	(2)
		Fiber	1.7, 1.6	(12)
		Fiber, as-spun	2.1	(4)
		Fiber, as-spun	3.2	(11)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Elongation at break	%	Heat-treated (600°C)	1.9	(11)
		Heat-treated (650°C)	1.3	(11)
		Fiber	1.9	(7)
		Fiber, heat-treated (value depends on MW)	1.1–1.8	(4)
		Fiber, as-spun	2.8	(13)
		Heat-treated (600°C)	1.7	(13)
		Heat-treated (665°C)	1.2	(13)
		Fiber, as-spun	3.2 ± 0.4	(14)
		Heat-treated (600°C)	1.9 ± 0.3	(14)
		Heat-treated (650°C)	1.3 ± 0.3	(14)
Compressive strength	GPa	Fiber	0.2–0.3	(5)
		Fiber	0.68	(4)
		Fiber	0.300 ± 0.035	(15)
Torsional modulus	GPa	Fiber	1.0	(5)
Persistence length Q	nm	300°C	20–30	(16)
Elastic moduli	GPa	C_{11}	16.33	(5)
		C_{12}	16.64	
		C_{13}	−0.49	
		C_{15}	−2.19	
		C_{22}	84.0	
		C_{23}	0.69	
		C_{25}	2.01	
		C_{33}	0.49	
		C_{35}	19.11	
		C_{44}	3.79	
		C_{46}	−4.18	
		C_{55}	14.10	
		C_{66}	10.34	
Coefficient of thermal expansion	ppm K^{-1}	Fiber	−7 to −10	(5)
Degradation temperature	K	Film, uniaxial	>873	(17)
Fiber flammability – critical oxygen concentration (COC)	–	Fiber	36.1 (top) 22.8 (bottom)	(2)
Apparent activation energy of polymerization	kcal mol^{-1}	–	7.16	(18)
Index of refraction	–	–		(4)
n_r			1.663	
n_t			1.589	
n_2			>3.0 (est.)	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Third-order nonlinear optical susceptibility $\chi^{(3)}$	esu	Nonresonant ($\lambda = 602$ nm)	$\sim 10^{-11}$	(19)
Raman (characteristic frequencies	cm^{-1}	–	1,615 1,540 1,280	(14)

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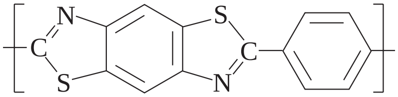
Poly(benzobisthiazole)

WILLIAM J. WELSH

ACRONYMS, ALTERNATIVE NAMES PBT, PBZT, poly(*p*-phenylene-2,6-benzobisthiazolediyl), poly[(benzo[1,2-d:4,5-d′]bisthiazole-2,6-diyl)-1,4-phenylene]

CLASS Rigid-rod polymers

STRUCTURE



MAJOR APPLICATIONS High-performance films, fibers, and coatings.

PROPERTIES OF SPECIAL INTEREST High-temperature resistance, unusual resistance to organic solvents, excellent mechanical properties, interesting electrical and nonlinear optical properties.

PREPARATIVE TECHNIQUES Polycondensation of a terephthalic acid with 2,5-diamino-1,4-benzenedithiol dihydrochloride in poly(phosphoric acid). Processing is primarily limited to variations of wet extrusion.(1)

SOLVENTS Protonic sulfonic acids RSO_3H, where R is $-OH$, $-CH_3$, $-Cl$, $-CF_3$, $-C_6H_5$, etc., and polyphosphoric acid (PPA).(1) Aprotic organic solvents (e.g., nitroalkanes) containing metal halide Lewis acids (e.g., $AlCl_3$, $GaCl_3$, $FeCl_3$) — up to 7.5% polymer.(2)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	As-spun fiber	1.47–1.53	(3)
		Heat treated fiber	1.54–1.60	(3)
		Model compound	1.44	(4)
		Film; uniaxial	1.56	(5)
		Film; balanced biaxial (quasi-isotropic)	1.56	(5)
		X-ray diffraction data	1.69	(6)
		X-ray diffraction data	1.713	(7)
		Microfibrils	1.46	(8)
		Fiber	1.58	(9)

Unit cell dimensions

Lattice	Monomers per unit cell	Cell dimensions (Å)			Cell angles (degrees)			Reference
		a	*b*	*c* (chain axis)	α	β	γ	
Monoclinic	1	5.83	3.54	12.35	90	90	96	(6)
Monoclinic	2	7.10	6.65	12.35	90	90	63	(6)
Monoclinic	2	11.957	3.555	12.35	90	90	100.9	(7)
Monoclinic	1	6.55	3.56	12.35	90	90	116.4	(7)
Monoclinic	2	11.790	3.539	12.514	90	90	94.0	(10)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Young's modulus	GPa	Fibers (25 mm)	18–331	(3)
		A-spun fiber	110	(11)
		Heat-treated fiber	280	(11)
		Ribbon	40	(12)
		Fiber	186	(13)
		Fiber	310	(14)
		Filaments, as-spun	17.0–159	(15)
		Filaments, heat-treated	303–331	(15)
		Fibers	200–330	(9)
		Fiber	320	(16)
		Film, uniaxial	270	(5)
		Film, balanced biaxial (quasi-isotropic)	34	(5)
Tensile strength	GPa	Fiber (25 mm)	2.35–4.19	(3)
		As-spun fiber	1.1	(11)
		Heat-treated fiber	2.7	(11)
		Ribbon	0.5	(12)
		Fiber	1.518	(13)
		Filament, as-spun	2.28–2.35	(15)
		Filament, heat-treated	3.49–4.19	(15)
		Fibers	3.0–4.2	(9)
		Fiber	3.1	(16)
		Film, uniaxial	2.0	(5)
		Film, balanced biaxial (quasi-isotropic)	0.55	(5)
Elongation at break	%	Fiber (25 mm)	1.3–7.1	(3)
		Filament, as-spun	2.4–7.1	(15)
		Filament, heat-treated	1.3–1.4	(15)
		Fiber	1.1	(16)
		Film, uniaxial	0.88	(5)
		Film, balanced biaxial (quasi-isotropic)	2.5	(5)
Compressive strength	GPa	–	0.3	(8)
		–	0.68	(3)
		Fibers	0.2–0.4	(9)
Torsional modulus	GPa	Fiber	1.2	(9)
Persistance length Q	nm	300°C	55–80	(17)
		CSA solvent	64.0 ± 0.9	(18)
Coefficient of thermal expansion	ppm K^{-1}	Film, uniaxial	-10	(5)
		Film, biaxial (quasi-isotropic)	-5	
Degradation temperature	K	Film, uniaxial	>873	(5)
		Film, biaxial (quasi-isotropic)	>873	(5)
		Fiber	~873	(19)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Fiber flammability – critical oxygen concentration (COC)	–	Fiber	35.7 (top) 22.6 (bottom)	(20)
Dielectric constant ε	–	Film, uniaxial Film, biaxial (quasi-isotropic)	2.8 2.8	(5)
Dissipation factor	–	Film, uniaxial Film, biaxial (quasi-isotropic)	0.005 0.005	(5)
Dielectric strength	volt mil^{-1}	Film, uniaxial Film, biaxial (quasi-isotropic)	8,900 8,900	(5)
Electrical conductivity	ohm^{-1} cm^{-1}	Electrochemically doped Undoped	$\sim$20 $\sim 10^{12}$	(21)
Cathodic peak	volts	Versus SCE	−1.70	
Anodic peak	volts	Versus SCE	−1.23	
Energy band gap	eV	Band edge at $\sim$500 nm	2.48	(22)
Index of refraction	–	Film ($\lambda = 602$ nm)	2.16	(23)
Optical loss α	cm^{-1}	Film	5.2×10^3	(23)
Third-order nonlinear optical susceptibility $\chi^{(3)}$	esu	Nonresonant ($\lambda = 602$ nm) – 1.3 μm	4.5×10^{-10} $\sim 10^{-11}$ 8.31 ± 1.66 ($\times 10^{-11}$)	(23) (24) (25)
Quantum efficiency	%	Solid state	6	(26)
IR (characteristic frequencies) (intensity)	cm^{-1}	Highly oriented film	3,076 (w); 3,076 (w); 3,027 (w); 1,605 (w); 1,532 (m); 1,500 (sh); 1,485 (vs); 1,428 (m); 1,410 (s); 1,401 (s); 1,314 (vs); 1,252 (s); 1,211 (w); 1,113 (m); 1,056 (m); 1,017 (w); 960 (vs); 860 (s); 837 (s); 732 (w); 705 (m); 689 (s); 627 (w); 605 (s); 488 (m)	(27)
Raman (characteristic frequencies) (intensity)	–	–	1,605 (s) 1,481 (s) 1,160–1,300 (m)	(28)
Wavelength at maximum of band	nm	UV-vis absorption in MSA	440	(29)
Birefringence	cm^{-1}	IR region	0.88 ± 0.04	(30)

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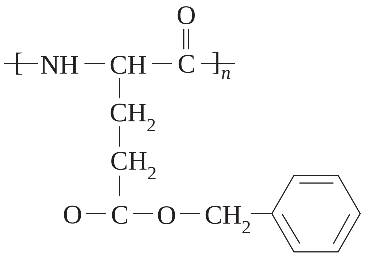
Poly(γ-benzyl-L-glutamate)

DOUGLAS G. GOLD AND WILMER G. MILLER

ACRONYM PBLG

CLASS Polypeptides and proteins

STRUCTURE



MAJOR APPLICATIONS Modeling of conformational changes of biopolymers and modeling of α-helical polypeptides. Used in chromatography as a stationary phase for the resolution of racemic materials. Microencapsulation of pharmaceutically active hydrophobic liquids. Improves shatter resistance of plastics when blended with poly(vinyl chloride), poly(vinyl acetate), or their copolymers.

PROPERTIES OF SPECIAL INTEREST Exists in a highly ordered, well-defined, α-helical conformation held intact by intramolecular hydrogen bonds. The α-helical structure renders the polymer as a relatively stiff rigid rod and is retained when the polymer is dissolved in many solvents. In these helicogenic solvents, PBLG exists as a single isotropic phase at low concentration. At higher concentrations a liquid-crystalline cholesteric phase is present.

COMMONS SOLVENTS AND NONSOLVENTS α-helical conformation when dissolved in solvents such as dimethylformamide, benzene, toluene, methylene chloride, and chloroform. Random coil conformation in trifluoroacetic acid (TFA) and dichloroacetic acid (DCA), and in mixed solvents containing TFA and DCA. Nonsolvents include water and methanol.

SYNTHESIS The first step involves the synthesis of the amino acid γ-benzyl-L-glutamate by a standard Fischer esterification reaction of L-glutamic acid with benzyl alcohol in the presence of strong acid. The amino acid is subsequently converted to the N-carboxyanhydride (NCA) monomer by reaction with phosgene gas,[1] or by reaction with the less hazardous compound triphosgene.[2] The NCA is polymerized by initiation with a variety compounds such as primary and secondary amines, and alkoxides.[1] Typical comonomers include other amino acid NCAs.

FRACTIONATION Fractionation has been accomplished using the following solvent/nonsolvent combinations: dichloroethane/petroleum ether, dioxane/ethanol, methylene chloride/methanol.[3]

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	219	—
Typical molecular weight range	$g\,mol^{-1}$	—	$10^4 - 3 \times 10^5$	—
Typical polydispersity index (M_w/M_n)	—	—	1.2	—
IR (characteristic absorption frequencies)	cm^{-1}	—	3,291; 1,733; 1,652; 1,550; 1,167	(1)
UV (characteristic absorption frequencies)	cm^{-1}	—	61,000; 53,800; 51,000; 47,800; 45,700	(1)
NMR	—	—	—	(1, 10)
Thermal expansion coefficients	K^{-1}	$T < T_g \approx 15°C$, buoyant-weight technique	2.3×10^{-4}	(4)
		$T > T_g \approx 15°C$, buoyant-weight technique	4.5×10^{-4}	
Second virial coefficient	$mol\,cm^3\,g^{-2}$	Dry DMF, 5–75°C, $M_w \sim 10^5$	4×10^{-4}	(5)
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None		K a	
		Dimethylformamide, 25°C, helical, 70,000–340,000	2.9×10^{-7} 1.7	(3)
		Dimethylformamide, 25°C, 60,000–570,000	5.6×10^{-6} 1.45	
		Dichloroacetic acid, 25°C, random coil, 20,000–340,000	2.78×10^{-3} 0.87	
		Dichloroacetic acid, 25°C, 60,000–570,000	8.8×10^{-3} 0.77	
Characteristic ratio	—	Dichloroacetic acid, 25°C, random coil	10.3	(3)
		m-Cresol, helical	400–622	(6)
Persistence length	Å	Helicogenic solvents	$1{,}100 \pm 500$	(6–8)
Theta temperature	K	Dichloroethane/diethylene glycol (80:20)	298	(3)
Density (crystalline)	$g\,cm^{-3}$	—	1.26–1.30	(3)
T_g-like transition temperature	K	Onset of side-chain rotation	288–293	(4, 9)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Shear modulus	MPa	25°C −40°C	1,000 7,000	(4)
Storage modulus	MPa	0°C, 0.1 Hz 25°C, 0.1 Hz	1,000 100	(9)
Loss modulus	MPa	0°C, 0.1 Hz 25°C, 0.1 Hz	100 30	(9)
WLF parameters: C_1 and C_2	°C (C_2)	—	$C_1 = -8.86$ $C_2 = 101.6$	(9)
Refractive index increment *dn/dc*	$ml\,g^{-1}$	Dichloroacetic acid, 25°C Dioxane, 25°C Dimethylformamide, 25°C, λ variable	0.085 0.114 0.118–0.127	(3) (1, 3) (5)
Optical activity $[\alpha]_D$	—	Chloroform dichloroacetic acid	$[\alpha]_{546} + 14$ $[\alpha]_{546} - 15$	(3)
Electronic band gap	eV	—	2.07	(1)
Conductance	$ohm^{-1}\,cm^{-1}$	—	2×10^{-17}	(1)
Piezoelectric coefficient	pCN^{-1}	—	−0.4	(1)
Magnetic susceptibility	$emu\,g^{-1}$	—	-0.52×10^{-6}	(1)
Surface tension	$mN\,m^{-1}$	20°C	39.2	(3)
Decomposition temperature	K	—	473	(1)
Helix pitch	Å	—	5.42	(1)
Axial translation per residue	Å	—	1.505	(1)
Residues per turn	—	—	3.6	(1)
Cost	$US\$\,g^{-1}$	25 mg–1,g	95	—
Availability	g	—	0.025–1	—
Suppliers	Sigma Chemical Co., P.O. Box 14508, St. Louis, Missouri 63178, USA. Polyscience Inc., 400 Valley Road, Warrington, Pennsylvania 18976, USA.			

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Poly(1,3-bis-*p*-carboxyphenoxypropane anhydride)

ABRAHAM J. DOMB AND ROBERT LANGER

ACRONYMS, TRADE NAMES BIODEL-CPP, Poly(CPP), Poly(CPP-SA)

CLASS Polyanhydrides

STRUCTURE $[-CO-C_6H_4-O-CH_2-CH_2-CH_2-O-C_6H_4-COO-]$

MAJOR APPLICATIONS Biodegradable polymer for controlled drug delivery in a form of implant or injectable microspheres (e.g., Gliadel^{TM}-BCNU-loaded wafer for the treatment of brain tumors).

PROPERTIES OF SPECIAL INTEREST Anhydride copolymers of 1,3-bis-*p*-carboxyphenoxypropane (CPP) with aliphatic diacids such as sebacic acid (SA) degrade in a physiological medium to CPP and SA. Matrices of the copolymers loaded with dissolved or dispersed drugs degrade in vitro and in vivo to constantly release the drugs for periods from 1–10 weeks.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight		P(CPP-SA)		
	10^4 g mol^{-1}	GPC-polystyrene standards	M_w = 3–20, M_n = 0.5–3	–
	dl g^{-1}	Viscosity 25°C, dichloromethane	η_{sp} = 0.2–0.9	–
IR (characteristic absorption frequencies)	cm^{-1}	Film on NaCl pellet	1,750, 1,810	(1)
		PSA	1,740, 1,770, 1,810	
		P(CPP-SA)	1,712, 1,773	
		P(CPP)		
Raman	cm^{-1}	Film on NaCl pellet		(1)
		PSA	1,739, 1,803	
		P(CPP-SA)	1,723, 1,765, 1,804	
		P(CPP)	1,712, 1,764	
UV (characteristic absorption wavelength)	nm	P(CPP-SA), dichloromethane	265	–
		CPP monomer, 1 N NaOH solution	265	
Optical rotation	–	Dichloromethane	No optical rotation	–

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Poly(1,3-bis-*p*-carboxyphenoxypropane anhydride)

PROPERTY	UNITS	CONDITIONS	VALUE				REFERENCE
Solubility	mg ml^{-1}		P(CPP-SA), 0–60 mol% CPP	P(CPP-SA), 70–100 mol% CPP			(2)
		Chloroform	>300	<1			
		Dichloromethane	>300	<1			
		Tetrahydrofuran	20	<1			
		Ketones	1	<1			
		Ethyl acetate	<1	<1			
		Alkanes and arenes	<1	<1			
		Ethers	<1	<1			
		Water	<1	<1			
Mark–Houwink parameters: K and a	ml g^{-1} None	$CHCl_3$, 23°C	$K = 3.88$ $a = 0.658$				(3)
Thermal properties		P(CPP-A), DSC, 10°C min^{-1}	0:100	22:78	46:54	100:0	(3)
	K	T_m	359.0	339.0	458.0	513.0	
	K	T_g	333.1	320.0	274.8	369.0	
	kJ kg^{-1}	ΔH	150.7	64.0	13.0	110.9	
Crystallinity	%	P(CPP-SA), powder, X-ray diffraction	0:100	22:78	46:54	100:0	(3)
		X_c	–	30.0	6.1	–	
		W_c	66.0	35.0	14.2	61.4	
Comonomer sequence distribution		P(CPP-SA), ^{1}H-NMR, $CDCl_3$	8:92	22:78	59:41	49:51	(3)
		Probability for SA-SA	0.86	0.61	0.36	0.24	
		Probability for SA-CPP	0.14	0.34	0.47	0.49	
		Average block length L(SA)	12.3	4.6	2.5	2.0	
		Degree of randomness	0.3	0.7	0.9	1.0	
Stability in chloroform solution (decrease in M_w) (anhydride interchange depolymerization)			P(CPP-SA)				(4)
			0:100	20:80	40:50		
Depolymerization rate constant	t^{-1}	37°C	0.1325	0.1535	0.0743		
Activation energy	kcal mol^{-1} K^{-1}		8.08	8.27	7.27		
Erosion rate	mg h^{-1}	P(CPP-SA), 14 × 1.2 mm disc, 0.1 M phosphate buffer, pH 7.4, 37°C	0:100	22:78	49:51	100:0	(5)
		SA	2.3	1.8	0.4	–	
		CPP	–	0.5	0.3	<0.01	

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Erosion front	$\mu m\ day^{-1}$	0.1 M phosphate buffer, pH 7.4, 37°C			(6)
		P(CPP-SA), 20:80	106 ± 5		
		P(CPP-SA), 50:50	118 ± 18		
Elimination in vivo	%		CPP	SA	(7)
		7 days in rat brain	2	95	
		21 days in rat brain	64	100	
Drug release in vitro	$\%\ day^{-1}$	P(CPP-SA), 20:80			(7)
		3.8% BCNU in disc	30		(6)
		5% indomethacin in disc	9		
Drug release in vivo	$\%\ day^{-1}$	3.8% BCNU disc implanted in rat brain	16		(7)
Biocompatibility	Compatible with human brain Compatible with rabbit brain, cornea, muscle, subcutane				(8)
Supplier	Guilford Pharmaceuticals, Inc., Baltimore, Maryland, USA				

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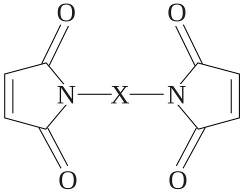
Poly(bis maleimide)

LOON-SENG TAN

ACRONYM BMI

CLASS Polyimides; thermoset resins; addition polyimides; composite matrix resins

STRUCTURE



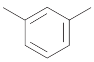
(X = aromatic or aliphatic bridging groups—see tables below)

MAJOR APPLICATIONS Printed circuit boards, laminating powder, carbon-fiber composites for aero-engines and military aircraft parts such as flap inboard cover, forward nozzle, gun pack, ammunition pack, blade choke, deep choke, speed brake, and ventral fin.[1]

PROPERTIES OF SPECIAL INTEREST BMI resins are generally brittle. They can be toughened with additives such aromatic diamines (chain extension via Michael Addition reaction), divinylbenzene or bis(allylphenyl) compounds (chain extension via Diels-Alder reaction and ene reaction, respectively), benzocyclobutene derivatives (chain extension via Diels-Alder reaction), low molecular weight rubber, and thermoplastics. Certain bismaleimides are liquid crystalline.[2]

SYNTHESIS Bismaleimides are generally prepared from the two-step reaction of maleic anhydride and diamines in the presence of acetic anhydride and catalytic amounts of nickel acetate and triethylamine.[3,4] Sodium acetate may be substituted for nickel acetate.[5] Poly(bismaleimides) are highly cross-linked polymers formed from thermally cured bismaleimides. Thermal curing can be promoted by either a radical-type initiator (peroxides or azo compounds)[6] or an ionic-type initiator such as 1,4-diazabicyclo-[2.2.2.]octane (DABCO), 2-methylimidazole[7] and triphenylphosphine.[8]

Thermal properties of bismaleimides*

LINKING GROUP (X)†	T_m (°C)	$T_{poly,max}$ (°C)	ΔH_{poly} (kJ mol^{-1})	REFERENCE
	363‡	–	–	(9)
	202–203	–	56.3	(10)

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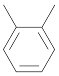
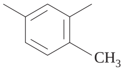
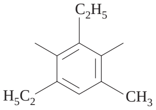
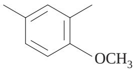
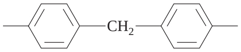
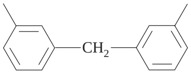
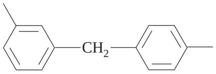
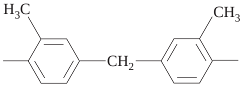
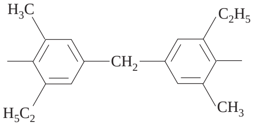
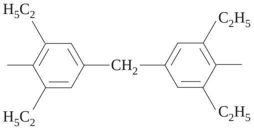
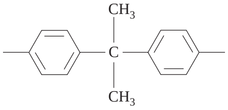
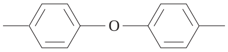
LINKING GROUP (X)[†]	T_m (°C)	$T_{poly,max}$ (°C)	ΔH_{poly} (kJ mol^{-1})	REFERENCE
	241	–	–	(11)
	174–176	–	50.8	(10)
	146–150	–	54.1	(10)
	174–175	–	61.1	(10)
	155–157	235	86.0	(10)
	–	–	70.9	(12)
	195–196	–	–	(13)
	164–165	–	–	(13)
	210–212	–	–	(12, 14)
	150–154	298	85.0	(10)
			82.7	(12)
	149–151	328	132	(10)
	–	–	96.9	(12)
	235	290	83.5	(12)
	172–178	286	57.6	(10, 12)

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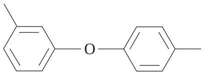
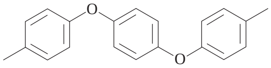
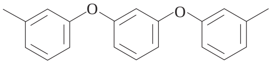
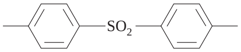
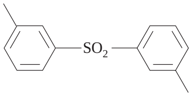
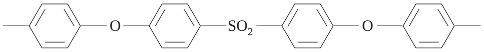
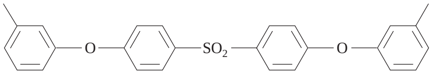
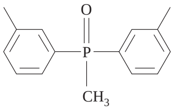
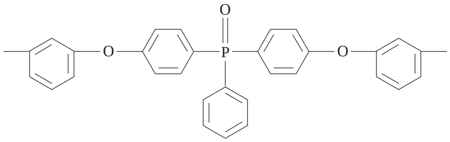
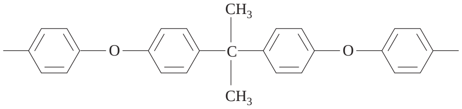
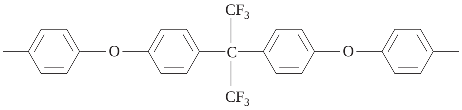
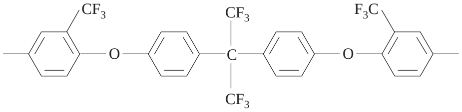
LINKING GROUP (X)[†]	T_m (°C)	$T_{poly,max}$ (°C)	ΔH_{poly} (kJ mol^{-1})	REFERENCE
	212	236	–	(11)
	239	252	84.6	(12)
	163 116	254 277	115 77	(12) (16)
	252–255	264	77.6 60.8	(10) (12)
	210–211 –	217 –	85.8 76.4	(10) (12)
	250	–	–	(12)
	80–92	295	114	(12)
	195	250	80	(11, 15)
	92	210	98.2	(16)
	83 142	270	56.6	(17)
	136	281	69.4	(17)
	112	323	66.5	(17)

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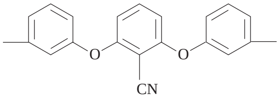
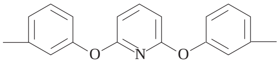
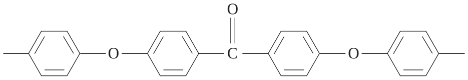
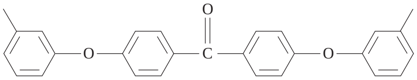
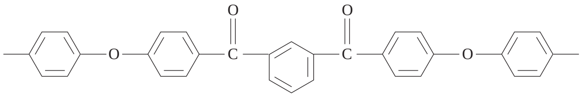
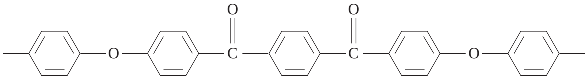
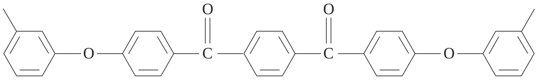
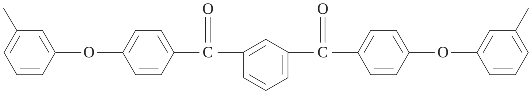
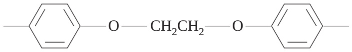
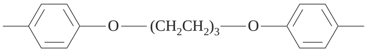
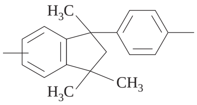
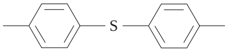
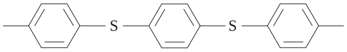
LINKING GROUP (X)[†]	T_m (°C)	$T_{poly,max}$ (°C)	ΔH_{poly} (kJ mol^{-1})	REFERENCE
	205	–	109	(19)
	137	258	186	(18)
	239	250	89–100	(12)
	85–91	304	123	(12)
	226	285 –	– 74.6	(12) (19)
	293	–	64.1	(19)
	209	–	104	(19)
	60–65 185	314 –	– 87.2	(12) (19)
	230	245	–	(20)
	176	274	–	(20)
	90–100	203	39.4	(4, 12)
	181–182	300	–	(11, 21)
	255–257	–	–	(21)

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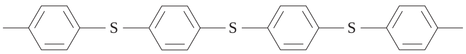
Poly(bis maleimide)

LINKING GROUP (X)[†]	T_m (°C)	$T_{poly,max}$ (°C)	ΔH_{poly} (kJ mol^{-1})	REFERENCE
	185–186	–	–	(21)
$-CH_2-C(CH_3)_2-CH_2-CH(CH_3)-CH_2-CH_2-$	70–130	–	–	(11)
$-(CH_2)_2-$	191–192	–	–	
$-(CH_2)_6-$	140–141.5	–	–	(22)
$-(CH_2)_8-$	123	–	–	(23)
	120–122	–	–	(22)
$-(CH_2)_{10}-$	113.5–115	–	–	(22)
$-(CH_2)_{12}-$	110–112	–	–	(22)

[*] T_m = normal melting temperature; $T_{poly,max}$ = maximum of polymerization exotherm; ΔH_{poly} = enthalpy of polymerization.
[†] X = an aromatic or aliphatic bridging group referred to in the structure shown at the beginning of this entry.
[‡] Decomposition temperature.

Typical physical properties of bis(4–maleimidophenyl)methane[(11, 24)]

PROPERTY	UNITS	CONDITIONS	VALUE
Physical form	–	–	Fine powder
Color	–	–	Yellow
Melting point	K	DSC	422–427
Exotherm peak temperature	K	DSC	533
Polymerization energy	J g^{-1}	DSC, heating rate at 20°C min^{-1}	>190

Properties of cured bis(4–maleimidophenyl)methane[(11, 24)]

PROPERTY	UNITS	CONDITIONS	VALUE
Glass transition temperature	K	DSC, heating rate at 20°C min^{-1}	503–563
Tensile strength	MPa	23°C	41–83
Tensile modulus	MPa	23°C	4–5 ($\times 10^3$)
Flexural strength	MPa	23°C	76–145
Flexural modulus	MPa	23°C	3.4–4.8 ($\times 10^3$)
Flexural strain to failure	%	23°C	1.3–2.3
Fracture energy	J m^{-2}	G_{IC}, 23°C	24–33

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Compimide 353* property data[10, 25]

PROPERTY	UNITS	CONDITIONS	VALUE
Melting point	K	–	341–402
Gel time	min	At 171°C	35–65
Viscosity	mPa	At 110°C	400–1,400
Polymerization exotherm, onset temperature	K	DSC, heating rate at 20°C min^{-1}	466 ± 10
Exotherm peak temperature	K	DSC, heating rate at 20°C min^{-1}	548 ± 15
Polymerization energy	$J\,g^{-1}$	DSC, heating rate at 20°C min^{-1}	220 ± 40

* A mixture comprising 50% of 1,4-bis(maleimido)diphenylmethane, 40% of 2,5-bis(maleimido)toluene, and 10% 1,6-bis(maleimido)-2,2-dimethyl-4-methyl-hexane.

Properties of compimide 353* neat resin castings[10, 25]

PROPERTY	UNITS	CONDITIONS	VALUE
T_g	K	–	>575
Flexural strength	MPa	At 24°C At 249°C	60 50
Flexural modulus	MPa	At 24°C At 249°C	5.5×10^3 3.4–3.5 ($\times 10^3$)
Fracture energy	$J\,m^{-2}$	At 24°C, G_{IC}	~25

* A eutectic mixture comprising 50% of 1,4-bis(maleimido)diphenylmethane, 40% of 2,5-bis(maleimido)toluene, and 10% 1,6-bis(maleimido)-2,2-dimethyl-4-methyl-hexane.

Range of properties of bismaleimides resins[26]

PROPERTY	UNITS	CONDITIONS	VALUE
Tensile strength	MPa	24°C 200°C	332–617 275–497
Tensile strain to failure	%	24°C 150°C	1.2–3.6 2.6
Flexural strength	MPa	24°C	121.3–166.8
Fracture toughness	$J\,m^{-1}$	At 24°C, GIC2	30–389

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PROPERTY	UNITS	CONDITIONS	VALUE
Glass transition temperature	K	–	478–593
Density	g cm^{-3}	24°C	1.22–1.30
Moisture absorption	wt%	–	1.0–4.8

Fracture toughness (G_{IC}) of some commercial BMI resins

BMI RESIN	UNITS	CONDITIONS	VALUE	REFERENCE
Kerimid 601	J m^{-2}	23°C	34	(27)
Kerimid 70003	J m^{-2}	23°C	82	(27)
Kerimid or Compimide 353	J m^{-2}	23°C	25	(27)
Compimide 795, 766, 800, 183	J m^{-2}	23°C	40–180	(27)
Modified Compimide 353	J m^{-2}	23°C	389	(27)
Desbimid	J m^{-2}	23°C	470	(28)
Ciba-Geigy Matrimid 5292 (XU292)	J m^{-2}	23°C	210, 259	(27)

Range of mechanical properties of graphite fiber/BMI composites (unidirectional)[26]

PROPERTY	UNITS	CONDITIONS	VALUE
Density	g cm^{-3}	60 vol% fiber and 40 vol% BMI	1.5–1.6
Flexural strength	MPa	24°C, dry 24°C, wet	1,916–2,047 1,930–2,041
Flexural strength	MPa	177°C, dry 177°C, wet 232°C, dry	1,930 1,378 1,234–1,378
Flexural modulus	MPa	24°C, dry 24°C, wet	124.1–144.1 ($\times 10^3$) 142.0×10^3
Glass transition temperature	K	DSC	478–593

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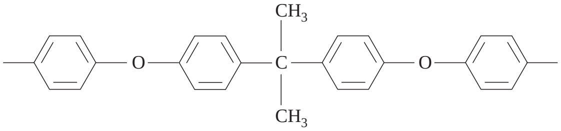
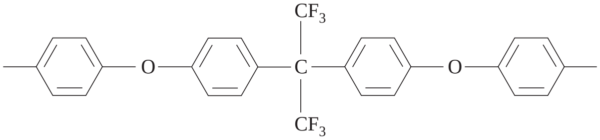
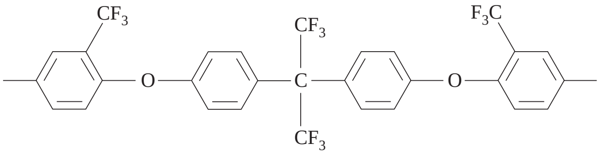
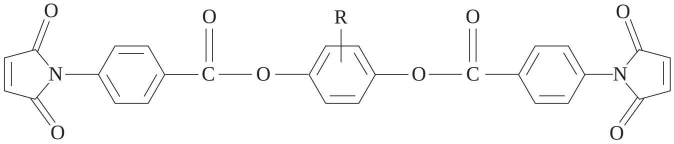
Dielectric constant values of some cured BMI[17]

X*	CONDITIONS	VALUE
	1 MHz, room temperature	3.2
	1 MHz, room temperature	3.0
	1 MHz, room temperature	2.8

* X = an aromatic or aliphatic bridging group referred to in the structure shown at the beginning of this entry.

Thermal properties of liquid crystalline, bismaleimide–based ester monomers*



R	TRANSITION TEMPERATURES† (°C)		
	Crystal to nematic ($k \rightarrow n$)	Nematic to isotropic ($n \rightarrow i$)	Thermosetting/Solidification
H	282	Not observed	293
CH_3	245	Not observed	280
Cl	215	Not observed	270

* Adapted from reference (2).
† Conditions: transition temperatures were determined by hot-stage, polarized light microscopy with a heating rate of approximately 20°C min^{-1}.

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Commercial BMI products

PRODUCT NAME	DESCRIPTION	SUPPLIERS
FM-32	Bismaleimide-based adhesives	American Cyanamid Co., Engineered Materials Department, 1300 Revolution Street, Havre de Grace, Maryland, USA
Cycom 3100	A proprietary BMI formulation for carbon fiber prepreg	
MR-54-4	A tough BMI resin formulation with cured T_g of 260°C, low water uptake, 180°C hot/wet service	Amoco Performance Products, Bound Brook, New Jersey 08805, USA
MR 56-2	A BMI resin formulation for high use temperature (T_g 350°C), for prepreg uses	
Narmco 5250-2, 5250-3, and 5250-4	Proprietary BMI prepreg resins; Narmco-5250-2 has the highest T_g and Narmco-5250-4 is the toughest of the series	BASF, Ludwigshafan, Germany; BASF, Structural Materials, Inc., Anaheim, California, USA
Vicotex 5564-1	A BMI formulation for autoclave molding	Brochier S. A. Lyon, France (a subsidiary of Ciba-Geigy)
Fibredux DLS 811, Fibredux 6451	Proprietary formulations for low-pressure autoclave molding	Ciba-Geigy, Composite Duxford, UK
Fiberite X86	A high-temperature BMI resin for laminates	ICI/Fiberite, Tempe, Arizona/Winona, Minnesota 55987/Greenwich, Texas 75401, USA
R6450, R6452, R6453	Proprietary BMI formulation	Ciba-Geigy, Composite Materials Division, Anaheim, California, USA
Matrimide 5292 A,B	A two-component resin system consists of 4,4′-bismaleimidodiphenylmethane (M5292A) and diallylbisphenol-A (M5292B)	Ciba-Geigy Corporation, Hawthorne, New York 10532, USA
RD85-101	A BMI resin derived from diaminodiphenyllindane and designed for hot-melt prepregging	
Araldite, XU5292	A BMI resin solution for printed circuit board applications	
Desmid	A BMI formulation, a mixture of 4,4′-diaminodiphenylmethane-based BMI (~50%), styrene, 2-hydroxyethylmethacrylate and a curing agent (trigonox HM)	DSM Advanced Composites, P.O. Box 18, 6160 MD Geleen, The Netherlands
MV-A2	A BMI building block derived from 1,3-diaminobenzene	Du Pont Company, Wilmington, Delaware, USA

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PRODUCT NAME	DESCRIPTION	SUPPLIERS
F 178	A first generation high T_g BMI resin formulation, for prepreg uses	Hexcel Corporation, Dublin, California, USA
F 650	A high-T_g BMI resin system, for prepreg uses	
F 652	A tough, controlled-flow BMI resin formulation for prepreg uses	
F 655	A controlled-flow, tough BMI system (for intermediate modulus fibers) for prepreg uses	
EA-9655	Bismaleimide-based adhesives	Hysol/Dexter Corporation, Pittsburg, California 94565, USA
EA-9673	BMI-based adhesives	
LR100-74	BMI-based adhesives	
BMI-70	BMI building block derived from bis(3-methyl-4-amino-5-ethyl-phenyl)methane	Ihara Chemical Industry Co.; Ken Seika Corporation
BT resins	Blends of bismaleimide (B) and triazine (T) resins, primarily for printed circuit board applications	Mitsubishi Gas Chemicals Co., Inc., Mitsubishi International Corporation, 520 Madison Avenue, 11th Floor, New York, New York 10022, USA
Bismaleimide-S	BMI building block derived from 4,4′-bismaleimidodiphenylmethane	Mitsui Toatsu Chemicals, Inc., Kasumigaseki, Chiyodaku, Tokyo, Japan; MTC America, Inc., New York, USA
IM-AD resins	A line of BMI resins designed for the manufacture of printed circuit boards, aerospace laminates, and structural composites	Reichhold Chemicals, Inc., Warren, New York 07060, USA
Kerimide 601	A resin system consists of a mixture of 1,1′-(4-methylene-1-phenylene)bismaleimide (BMPM) and methylene dianiline (MDA) in a BMPM:MDA molar ratio of 2.5 : 1	Rhone-Poulenc Chimie, Lyon, France; Rhone-Poulenc, Inc., Seattle, USA
Kerimid 353	A tacky mixture of three BMIs; melts at 70–125°C; low resin viscosity at 125°C allows for rapid and thorough fiber impregnation	
Rhodmid M3	A BMI resin derived from 4,4′-bismaleimidodiphenylmethane	

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PRODUCT NAME	DESCRIPTION	SUPPLIERS
Compimide MDAB	A BMI building block based on 4,4′-bismaleimidodiphenylmethane	Shell Chemical Company, Houston, Texas 77252, USA;
Compimides 353, 353A, 796	A basic hot-melt type, eutectic mixture of BMI based on methyldianiline and aliphatic diamines	Technochemie GmbH-Verfarenstechnik, Dossenheim, Germany;
Compimide 15MRK	A formulated BMI resin for injection and compression molding	Deutche Shell Chemie GmbH, Eschhorn, Germany
Compimide 65 FWR	A filament windable BMI resin	
Compimide 1206-F55	A 50–60% by weight solution of BMI resin for prepregging	
V378A	A high-T_g hot/wet resistant resin	U. S. Polymeric, Santa Ana, California;
V390	A toughened high-T_g BMI formulation	Hitco Materials Division;
V398	A tough BMI system	BP Chemicals (Hitco) Inc., Anaheim, California
V391	A BMI thermoset with thermoplatic-like toughness	

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1,2-Polybutadiene

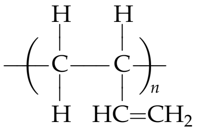
RAHUL D. PATIL

CLASS Diene elastomers; diene polymers

CAS REGISTRY NUMBER [26160-98-5]

SYNDIOTACTIC [31567-90-5]

STRUCTURE



MAJOR APPLICATIONS With one chiral center, 1,2-polybutadiene can exist in the amorphous atactic form and two crystalline forms: isotactic and syndiotactic. In the formation of 1,2-polybutadiene, it is believed that the syn *p*-allyl form yields the syndiotactic structure, while the anti *p*-allyl form yields the isotactic structures. The equilibrium mixture of syn and anti *p*-allyl structures yields heterotactic polybutadiene. At present, the two stereo-isomers that are most used commercially are the syndiotactic and heterotactic structures.(1)

COMMERCIAL USE Syndiotactic 1,2-polybutadiene is used in films, footwear soles, tubes, and hoses; atactic 1,2-polybutadiene is extensively used in the rubber and tire industry.(1,2)

PROPERTIES OF SPECIAL INTEREST Syndiotactic 1,2-polybutadiene is a reactive thermoplastic resin, which has characteristics of both a thermoplastic and an elastomer.(1,2)

PREPARATION The preparation of amorphous high (99%) 1,2-polybutadiene was first reported in 1981.(3) Several reports in the literature describe the preparation of low, medium, and high vinyl 1,2-polybutadienes.(1,4,5) Syndiotactic 1,2-polybutadiene can be prepared using various cobalt catalysts.(1,6–9)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Average molecular weight M_w	g mol^{-1}	Syndiotatic	100,000	(10)
Specific gravity	g cm^{-3}	92% 1,2 content	0.902	(11)
Melting temperature	K	Syndiotactic Isotactic Atactic	429 399 —	(12)
Glass transition temperature	K	Syndiotactic Isotactic Atactic	245 — 269	(12)
Solubility parameter	(MPa)$^{1/2}$	90% 1,2- units	17.4	(13)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Mark-Houwink parameters: *K* and *a*	$K = \text{ml g}^{-1}$ $a =$ None	In toluene	$K = 9.01 \times 10^{-5}$ $a = 0.81$	(14)
Intrinsic viscosity	dl g^{-1}	In benzene at 30°C	1.52	(15)
Infrared absorption coefficients	$(\text{dl cm}^{-1}\text{ mg}^{-1}) \times 10^{-3}$	Wave length (mm) 10.35 10.95–10.98 13.5–13.65	 0.828 26.7 0.231	(16)
Infrared absorption coefficients	$\text{mol}^{-1}\text{ cm}^{-1}$	Wave length (mm) 10.3 11.0 12–15.75	 6.7 184 4.7	(17)
Water contact angle	degrees	At pH 1 At pH 12	95 97	(10)
Critical surface tension	$(\text{Nm}^{-1}) \times 10^3$	–	25	(18)
Refractive index	–	–	1.51	1
Solubility	–	In THF at 25°C In toluene at 25°C	Soluble Soluble	(14)

Unit cell dimensions[19–22]

Isomer	Lattice	Monomers per unit cell	Cell dimensions (Å)			Cell angles (degrees)		
			a	*b*	*c* (chain axis)	α	β	γ
Isotactic (99%)	Rhombohedral	18	17.3	17.3	6.5	90	90	120
Syndiotactic (98%)	Orthorhombic	4	10.98	6.60	5.14	90	90	90

Parameters of internal rotation[13]

1,2 content (%)	*C*	*s*	*U*	U_0 (J mol^{-1})	ε
30	2.32	1.67	1.40	2385	0.83
50	2.34	1.83	1.55	2427	0.97
66	2.41	1.89	1.55	2469	1.06
90	2.41	2.05	1.79	2469	1.20

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Molecular weight and intrinsic viscosity*[13]

$[\eta]$ (dl g^{-1})	$M_w \times 10^{-4}$
1.40	20.12
1.98	30.94
2.45	41.66
2.74	49.20
3.40	68.41
4.27	92.92

* For 90% 1,2- and 10% *trans*, intrinsic viscosity was measured in toluene at 30°C ± 0.05°C.

Microstructure and properties of syndiotactic 1,2-polybutadiene[23]

mp (°C)	Heat of fusion (J g^{-1})	Crystallinity (%)	$[\eta]$ (dl g^{-1})	^{1}H-NMR 1,2 content (%)	^{13}C-NMR (%)	
					1,2 content	Syndiotactic
210	78.7	77.5	6.06	99.72	99.0	99.6
208	77.4	79.7	5.08	99.74	99.2	99.4
206	75.7	81.7	2.00	99.02	98.8	98.8
202	74.5	77.2	1.94	97.75	96.8	97.9
200	79.5	78.3	1.11	97.28	96.0	97.8
192	76.6	72.2	0.46	95.35	93.6	95.1
156	45.2	55.6	0.12	86.27	83.2	87.7

Mechanical properties[11]

PROPERTY	UNITS	CONDITIONS	VALUE
Tensile strength	MPa	–	11.2
Elongation	%	–	650
M300 stress at 300%	MPa	–	6.9
Tear strength	kN m^{-1}	–	68.8
Yield stress	MPa	–	5.6
Hardness	Shore D	–	35
Impact strength	$(J\,m^{-1}) \times 10^{-3}$	–	5.0
Tension set	%	At 100% elongation At break	22 145
Hysteresis loss	–	At 30% strain At 300% strain	0.177 0.772

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Properties of syndiotactic-PB fibers[24]

mp (°C)	Stretching temp. ratio	Diameter (μm)	Initial modulus (t cm^{-2})	Tenacity (t cm^{-2})	Elongation (%)	Birefringence $\Delta \times 10^3$
187	60 × 1.8	14.5	11.4	1.50	68	−11.5
185	60 × 2.1	14.4	16.7	2.25	19	−12.1
192	60 × 2.3	14.0	16.9	1.61	18	−13.6

Literature available

1,2-polybutadiene	Reference
Conformational properties	(25)
Effects of fillers on mechanical and viscoelastic properties	(11)
Infrared laser-induced reactions with difluorovinylidene	(26)
Adhesion and wettability studies	(18, 27)
Radiation induced addition of carbon tetrachloride	(28)
Hydrogenation	(29, 30)

Suppliers

1. Scientific Polymer Products, Inc., 6265 Dean Parkway, Ontario, New York 14519-8997, USA
2. Acros Organics USA, 711 Forbes Avenue, Pittsburgh, Pennsylvania 15219-4785, USA
3. Niss America, Inc., 220E 42nd Street, Suite 3002, New York, New York 10017, USA

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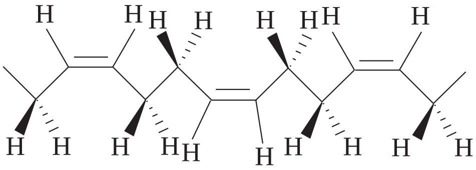
cis-1,4-Polybutadiene

M. A. SHARAF

CLASS Diene elastomers

STRUCTURE



MAJOR APPLICATIONS Tires and tire products, sealants, belts, gaskets, hoses, automotive molded articles, rubber bands, gloves, footware, sporting goods, and rubber sheeting. Block copolymers with styrene are used for adhesives and footware.

PROPERTIES OF SPECIAL INTEREST High green strength, tack, can be compounded with fillers and other polymers, can form block copolymers for specialty applications, high tensile strength owing to strain-induced crystallization.

Preparative techniques

CATALYST SYSTEMS	MICROSTRUCTURE (%)			REFERENCE
	CIS-1,4	*TRANS*-1,4	1,2-VINYL	
Ziegler-Natta				
AlR_3/TiI_4	92	3	5	(1–4)
$AlR_3/TiI_4O(i-C_3H_7)_2$	92–94	2-3	5	(5)
$AlR_3/TiCl_4/TiI_4$	93–94	2-3	4	(6, 7)
$AlR_2Cl/Co(acac)_2/2H_2O$	98	≈1	≈1	(8–15)
$AlR_3/Ni(OCOR)_2/BF_3O(C_2H_5)_2$	97	≈1.5	≈1.5	(16, 17)
$Al(C_2H_5)_2Cl/Nd(OCOR)_3/AlR_3$	98–99	–	≈1	(18-21)
$AlR_3/NdCl_3$/Donor	99	–	≈1	(20, 21)
η3-Allyl derivatives of transition metals				
(η3-C_4H_7)$CrOCOCl_3$	93	4	3	(22, 23)
(η3-C_4H_7)$CrCl_2$	90	5	5	(23)
(η3-C_4H_7)CoCl	91	2	7	(23)
(η3-C_4H_7)$NiCl_2$	85–90	5–10	–	(24, 25)
(η3-C_4H_7)$NiOC_6H_2(NO_2)_3$	97	3	–	(26)
(η3-C_4H_7)$NiOCOCF_3$	91–98	1–8	1	(26, 27)
(η3-$C_{12}H_{19}$)$NiOCOCF_3$	98	2	–	(28)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of polymerization	kJ mol^{-1}	*Cis*-1,4- addition at 25°C	78	(29)
Entropy of polymerization	J K^{-1} mol^{-1}	*Cis*-1,4- addition at 25°C	84	(30)
Activation energy of thermal depolymerization	kJ mol^{-1}	—	259	(31)
Major infrared bands	cm^{-1}	In phase out-of-plane CH wag	730	(32)
		CH_2 wag	1,310	
		C=C stretching	1,655	
Infrared absorption coefficients	dl cm^{-1} mg^{-1} ($\times 10^{-3}$)	In phase out-of-plane CH wag, 740 cm^{-1} (shift to 725 cm^{-1} for lower content of *cis*-1,4- units)	5.73	(33–37)
Infrared molar absorptivities	mol^{-1} cm^{-1}	In phase out-of-plane CH wag, 740 cm^{-1} (shift to 725 cm^{-1} for lower content of *cis*-1,4- units)	10.1	(32–38)
High resolution ^{1}H NMR resonance lines				
Proton resonance lines	ppm	250 MHz or greater		(39, 40)
		1,2 methylene	1.3	
		1,4 methylene (occurs as doublet corresponding to *cis-trans* units)	2.0	
		1,2 terminal vinyl	4.8	
		1,4 olefinic (occurs as doublet corresponding to *cis-trans* units)	5.4	
		1,2 nonterminal vinyl	5.6	
Solid state proton resonance lines	ppm	1,4 methylene	25	(41)
		1,4 olefinic		
^{13}C resonance lines	ppm	In $CDCl_3$ at 40°C		(42–46)
		1,4 methylene	≈27.5	
		1,4 olefinic	129	
^{13}C T_1	s	In $CDCl_3$ at 54°C	3	—
^{13}C correlation time	ns	In $CDCl_3$ at 54°C	0.01–0.016	(47)
Schaefer width parameter p	—	Methylene carbon, $T = 40$–45°C	9	(47)
J-coupling constant (^{13}C satallite signal of olefinic protons)	Hz	55°C	10.7	(48)
Neutron scattering length density	10^{14} m^{-2}	23°C	0.41	(49)
Density	g cm^{-3}	1,4-*cis*	0.915	(50)
		1,4-*cis* (98–99%), 5°C	1.01	(51)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Reducing paremeters for the Simha-Somcyncky equation of state: T^*, V^*, P^*	$T^* = \text{K}$ $V^* = \text{cm}^3\,\text{g}^{-1}$ $P^* = \text{MPa}$	T-range = 5–55°C, P-range = 0–300 MPa	$T^* = 9,644$ $V^* = 1.0861$ $P^* = 771.4$	(52)

Theta solvents and temperatures

Cis units (%)	Solvent	θ Temp. (K)	Method	Reference
97	*n*-Heptane	272	Phase equilibria	(53)
97	*n* -Propyl acetate	308.5	Virial coefficient, viscosity	(53)
97	5-Methyl-2-hexanone/2-pentanone (1/3 V)	319.2	Phase equilibria	(54)
97	5-Methyl-2-hexanone/2-pentanone (1/1 V)	305.7	–	(54)
97	5-Methyl-2-hexanone/2-pentanone (3/1 V)	295.3	–	(54)
97	3-Pentanone	283.3	–	(54)
97	3-Pentanone/2-pentanone (3/2 V)	303.0	–	(54)
94	Diethyl ketone	486	–	(55)
94	Ethyl propyl ketone	513	–	(55)
94	Propylene oxide	419	–	(55)
93	Diethyl ketone	287	–	(55)
93	Diethyl ketone	481	–	(55)
93	Ethyl propyl ketone	251	–	(55)
93	Ethyl propyl ketone	510	–	(55)
93	Propylene oxide	308	–	(55)
93	Propylene oxide	414	–	(55)
90	*i*-Butyl acetate	293.5	Virial coefficient, viscosity	(56)
90	*n*-Heptane/*n*-hexane (50/50 V)	278	Phase equilibria	(57)
90	*n*-Heptane/*n*-hexane (25/75)	293	–	(57)
90	5-Methyl-2-hexanone	285.6	–	(58)
90	2-Pentanone	332.7	–	(58)
90	3-Pentanone	283.6	–	(58)

Second virial coefficient[59]

Solvent	Temp. (°C)	$M \times 10^{-5}$ (g mol^{-1})	Condition	Method	$A_2 \times 10^{10}$ (mol m^3 g^{-2})
Benzene	28.6	0.6–2.93	–	Osmometry	15.3
		1.38	–		27.9
Cyclohexane	28.6	8.4–43.5	Unfractionated sample	Light scattering	2.92
		1.43–1.64	Fractionated sample		7.5–1.63

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PROPERTY	CONDITIONS	VALUE	REFERENCE
Solvents	Hydrocarbons, tetrahydrofuran, higher ketones, higher aliphatic esters		(60, 61)
Nonsolvents	Alcohol, lower ketones, lower esters, nitromethane, proponitrile, water, dilute acids, dilute alkalies, hypochlorite solutions		(60, 61)
Solvent/nonsolvent mixtures	Benzene/acetone, benzene/*n*-butanol, benzene/*n*-methanol, chloroform/acetone, dichloroethane/2-butanone, toluene/*n*-butanol, toluene/methanol	Fractional precipitation	(61)
	Amyl acetate/2-ethoxy ethanol, benzene/methanol, acetone, (acetone, *n*-hexane)	Fractional solution	
	Benzene/methanol, carbon tetrachloride/*n*-butanol	Turbidimetric titration	

Super critical fluids[62, 63]

Mol. wt. ($g\,mol^{-1}$)	Solvent	Temp. (°C)	Pressure (MPa)	Conc. (wt%)	Method	Conditions
5,000	CO_2	25	19.3	0.27	Cloud point	*Cis*-1,4

Unit cell dimensions[50, 64–68]

Isomer	Lattice	Space group	Monomer per unit cell	Density, cryst. ($g\,cm^{-3}$)	Melting point T_m (°C)	Unit cell dimensions (Å)			Cell angles (degrees)		
						a	*b*	*c* (chain axis)	α	β	γ
1,4-*cis* (98–99%)	Monoclinic	CS-4	4	1.012	1	4.6	9.5	8.6	90	109	90

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of fusion	$kJ\,mol^{-1}$	1,4-*cis*	2.51	(69)
			9.2 ± 0.5	(70)
Entropy of fusion	$J\,K^{-1}\,mol^{-1}$	1,4-*cis* (98%)	33.5	(71)
Glass transition temperature	K	1,4-*cis*	167	(69)
		1,4-*cis*	171	(71)
		1,4-*cis* (98–99%)	178	(72)
Melting temperature	K	1,4-*cis* (98–99%)	275	(50, 73)
		1,4-*cis* (98.5%)	274	(52)
		–	285	(68)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	Unspecified microstructure, $T = 20°C$	0.22	(73)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Coefficient of thermal expansion	$K^{-1} \times 10^{-4}$	Unspecified microstructure, $T = 25°C$	6.7 1.5	(74) (75)
Compressibility	$P^{-1} \times 10^{-10}$	Estimated, unspecified microstructure	7.25	(74)
Cohesive energy density	$(J\,m^{-3})^{1/2} \times 10^3$	*Cis*-1,4	16.85	(76)
Solubility parameters δ	$(MPa)^{1/2}$	Polybutadiene, unspecified microstructure	16.57 17.08 14.65–17.6	(77) (78) (79)
		Different solvents	—	(77, 79)
Huggins coefficients: $[\eta]$ and k'	—	*Cis*; toluene; 25°C	$[\eta] = 2.52$ $k' = 0.33$	(80)
Heat capacity C_p	$J\,K^{-1}\,mol^{-1}$	94% *cis*, 3% *trans*, 3% vinyl 1,2	See table below	(81, 82)

Temp. (K)	C_p	Condition	T_g (K)	$(\Delta C_p)_{T_g}$	T_m (K)	$(\Delta C_p)_{T_m}$
10	1.18	Solid	171	29.1	284	86.78–103.1
50	19.98	Solid	—	—	—	—
100	34.63	Solid	—	—	—	—
150	48.5	Solid	—	—	—	—
300	106.00	Melt	—	—	—	—
350	114.9	Melt	—	—	—	—

Polymer-solvent interaction parameter χ

Solvent	υ_2*	χ	Conditions	Method	Reference
n-Heptane	—	$0.45 + 0.35\upsilon_2$	—	—	(83)
Benzene	—	0.21	98% *cis* units	Vapor sorption	(84)
		0.325	Unspecified *cis* content	—	(85)
Benzene	0.0995	0.253	$\nu_{eff} = 136^{\dagger}$	Calculated from stress-strain and swelling meaurements on networks	(86)
Decane	0.256	0.477			
Benzene	0.0679	0.275	$\nu_{eff} = 64^{\dagger}$	—	(86)
Decane	0.191	0.477			
Benzene	0.08	0.292	$\nu_{eff} = 79^{\dagger}$	—	(86)
Decane	0.186	0.445			
Hexadecane	0.304	0.545			
Benzene	0.0588	0.28	$\nu_{eff} = 48.2^{\dagger}$	—	(86)
Decane	0.155	0.453			
Hexadecane	0.256	0.538			

*υ_2 = volume fraction of polymer.
†ν_{eff} = number density of elastically effective chains (mol m^3).

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cis-1,4-Polybutadiene

Mark-Houwink parameters: *K* and *a*

Microstructure			Solvent	Temp. (°C)	Mol. mass range ($M \times 10^{-5}$)	Conditions	Method	*K* (ml g^{-1})	*a*	Reference
% *Cis*	% *Trans*	% Vinyl 1,2								
98	0	2	Benzene	30	5	—	Osmometry	0.0337	0.715	(56)
			Isobutyl acetate	20.5	0	θ solvent	Osmometry	0.185	0.5	(56)
			Toluene	30	5	—	Osmometry	0.0305	0.725	(56)
95	1	4	Benzene	30	5	—	Light scattering	0.0085	—	(87)
			Cyclohexane	30	5	—	Light scattering	0.0112	—	(87)
			5-Methyl-2-hexanone	12.6	—	θ solvent	Light scattering	0.15	—	(88)
			3-Pentanone	10.3	—	θ solvent	Light scattering	0.152	—	(88)
			Toluene	30	—	—	Osmometry	0.0339	—	(89)
94	4	2	Benzene	—	—	—	Osmometry	0.0414	—	(90)
			Dioxane	20.2	12	θ solvent	Osmometry	0.205	—	(90)
92	3	5	Benzene	32	16	θ solvent	Light scattering	0.01	0.77	(59)

Unperturbed dimensions, $\langle r \rangle_0 / M^{1/2}$, and characteristic ratios, C_∞

Microstructure			Solvent	Temp. (°C)	Conditions	Method	$\langle r \rangle_0 / M^{1/2} \times 10^4$ (nm)	C_∞	Reference
% *Cis*	% *Trans*	% Vinyl 1,2							
100	0	0	Dioxane	20.2	θ solvent	Viscosity	920	5.15	(90)
98	0	2	Isobutyl acetate	20.5	—	Viscosity	880	4.75	(56)
95	0	5	2-Pentanone	59.7	—	Viscosity	835	4.3	(88)
			3-Pentanone	10.3	—	Viscosity	825	4.2	(88)

Temperature coefficients of unperturbed mean squared end-to-end distance, $d\ ln\langle r^2 \rangle_0 / dT$; and energetic contribution to total elastic force, f_e/f

% *Cis* units	Solvent	Temp. (°C)	Deformation α	$d\ ln\langle r^2 \rangle_0 / dT \times 10^3$ K^{-1}	f_e/f	Conditions	Method	Reference
94	Undiluted	50–90	1.25	0.4	0.12	Peroxide cure	Stress-temperature, elongation	(91)
			1.34	0.36	0.12	—		(91)
			1.35	0.24	0.08	β-Radiation		(91)
—	Undiluted	25–65	0.95	0.43	0.14	γ-Radiation; cross-linking in solution of toluene	Stress-temperature, compression	(91)
			0.9	0.45	0.14			(91)
			0.85	0.48	0.15			(91)
—	1-Chloronaphthalene	—	0.9	0.41	0.13	—	—	(91)
			0.85	0.44	0.14	—	—	(91)
			0.8	0.47	0.15	—	—	(91)
			0.75	0.51	0.16	—	—	(91)
96	—	—	—	0.31	0.1	—	—	(92)
96	—	—	—	0.41	0.12	—	—	(93)

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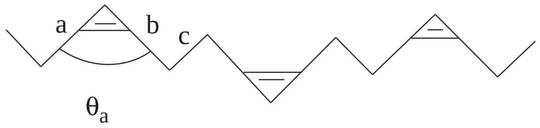
Rotational isomeric state (RIS) parameters and matrices(94)*



	u_i	u_0	E_0 (kJ mol^{-1})	Conditions
γ	10	1	−6.7	343 K
σ	1.4	1	−0.8	—

$u_a =$

	t	s$^+$	g$^+$	*c*	g$^-$	s$^-$
t	1	1	0	0	0	1
s$^+$	0	0	0	0	0	0
g$^+$	1	1	0	0	0	1
c	0	0	0	0	0	0
g$^-$	1	1	0	0	0	1
s$^-$	0	0	0	0	0	0

$u_b =$

	t	s$^+$	g$^+$	*c*	g$^-$	s$^-$
t	0	1	0	0	0	1
s$^+$	1	γ	0	0	0	γ
g$^+$	0	0	0	0	0	0
c	0	0	0	0	0	0
g$^-$	0	0	0	0	0	0
s$^-$	1	γ	0	0	0	γ

$u_c =$

	t	s$^+$	g$^+$	*c*	g$^-$	s$^-$
t	1	0	σ	0	γ	0
s$^+$	1	0	γ	0	γ	0
g$^+$	0	0	0	0	0	0
c	0	0	0	0	0	0
g$^-$	0	0	0	0	0	0
s$^-$	1	0	γ	0	γ	0

*Further RIS work on *cis*-1,4-polybutadiene can be found in references (95–98).

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Refractive index	—	*Cis*-1,4, 25°C	1.526	(99)
			1.5	(100)
Refractive index increment *dn*/*dc*	ml g^{-1}	1,4- units, 25°C, cyclohexane		(101)
		$\lambda = 436$ nm	0.121	
		$\lambda = 546$ nm	0.113	
Molar polarizability α	m$^3 \times 10^{-31}$	*Cis*-1,4	71.4	(99)
Directional polarizabilities	m$^3 \times 10^{-31}$	96% *cis*, undiluted		(102)
		b_{xx}	93.52	
		b_{yy}	77.19	
		b_{zz}	50.90	

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Optical segmental anisotropy $(\alpha_1 - \alpha_2)$ and optical anisotropy of monomer units $(b_l - b_t)$	$m^3 \times 10^{-31}$	Swollen polymer networks	$(\alpha_1 - \alpha_2)$	$(b_l - b_t)$	
		Benzene	61.3–63	30.8	(90, 103, 104)
		Carbon tetrachloride	53.5	31.7	(104)
		Carbon tetrachloride	55.2	–	(103)
		Cyclohexane	57.3	33.9	(104)
		Toluene	72	42.6	(104)
		p-Xylene	86.9	51.4	(104)
		Undiluted	77.7	29.2	(102)
Temperature coefficient of segmental anisotropy, $R\,d\ln(\alpha_1 - \alpha_2)/d(1/T)$	$kJ\,mol^{-1}$	96% *cis* units	0.355		(102)
Surface tension	$mN\,m^{-1}$	*Cis*-1,4	32		(105)

Sedimentation coefficient, s_0, and diffusion coefficient, D_0

% *Cis* units	Solvent	Temp. (°C)	Mol. mass, $M \times 10^{-5}$ ($g\,mol^{-1}$)	$s_0 \times 10^{13}$ (s^{-1})	$D_0 \times 10^{11}$ ($m^2\,s^{-1}$)	Conditions	Reference
94	Diethylketone	10.3	–	$0.53 \times 10^{-15} M^{0.5}$	–	θ solvent	(106)
90	Hexane/heptane (1:1)	20	0.5–10.8	$2.80 \times 10^{-15} M^{0.48}$	–	TiI_4 catalyst system	(57)
90	Hexane/heptane (1:1)	20	0.35–10.4	$2.33 \times 10^{-15} M^{0.5}$	–	$CoCl_2$ catalyst system	(57)
High	Hexatriacontane	80	–	–	4.78	–	(107)
High	Dodecane	80	–	–	23.8	–	(107)
High	Hexaflourobenzene	80	–	–	16.3	–	(107)

PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Transport of gases		Permeant	Temp. (°C)	Temp. range (°C)		(75, 108, 109)
Permeability coefficient P	m^3 (STP) $m\,s^{-1}\,m^{-2}\,Pa^{-1} \times 10^{-17}$	N_2	25	25–50	4.84	
		O_2	–	25–50	14.3	
		CO_2	–	25–50	104	
		He	24	0–45	24.5	
		Ne	–	0–45	14.4	
		Ar	–	0–45	30.8	
		N_2	–	0–45	14.4	
Preexponential factor P_0	m^3 (STP) $m\,s^{-1}\,m^{-2}\,Pa^{-1} \times 10^{-17}$	N_2	25	25–50	4.91	
		O_2	–	25–50	2.27	
		CO_2	–	25–50	0.683	
		He	24	0–45	0.0855	
		Ne	–	0–45	0.096	
		Ar	–	0–45	0.084	
		N_2	–	0–45	0.078	

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Transport of gases		Permeant	Temp. (°C)	Temp. range (°C)		
Diffusion coefficient D	$m^2 s^{-1} \times 10^{-10}$	N_2	25	25–50	1.1	
		O_2	–	25–50	1.5	
		CO_2	–	25–50	1.05	
		He	24	0–45	15.7	
		Ne	–	0–45	6.55	
		Ar	–	0–45	4.06	
		N_2	–	0–45	2.96	
Solubility coefficient S	m^3 (STP)m^{-3} $Pa^{-1} \times 10^{-6}$	N_2	25	25–50	0.444	
		O_2	–	25–50	0.957	
		CO_2	–	25–50	9.87	
		He	24	0–45	0.156	
		Ne	–	0–45	0.220	
		Ar	–	0–45	0.758	
		N_2	–	0–45	0.488	
Activation energy of permeation E_p	$kJ\,mol^{-1}$	N_2	25	25–50	34.3	
		O_2	–	25–50	29.7	
		CO_2	–	25–50	21.8	
		He	24	0–45	20.3	
		Ne	–	0–45	21.8	
		Ar	–	0–45	19.4	
		N_2	–	0–45	21.3	
Activation energy of diffusion E_D	$kJ\,mol^{-1}$	N_2	25	25–50	30.1	
		O_2	–	25–50	28.5	
		CO_2	–	25–50	30.6	
		He	24	0–45	17.3	
		Ne	–	0–45	17.4	
		Ar	–	0–45	21.3	
		N_2	–	0–45	25.0	
Heat of solution E_S	$kJ\,mol^{-1}$	N_2	25	25–50	4.2	
		O_2	–	25–50	1.2	
		CO_2	–	25–50	−8.8	
		He	24	0–45	2.9	
		Ne	–	0–45	4.4	
		Ar	–	0–45	−1.9	
		N_2	–	0–45	−3.7	
Heat of solution E_s	$kJ\,mol^{-1}$	–			2.9	(109)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Activation energy of viscous flow	$kJ\,mol^{-1}$	Uspecified microstructure	33.4–41.8	(75)
Rheological properties		96% *cis*- units, T = 25°C		(110)
Plateau modulus G_N°	MPa		0.76 0.73 (calculated)	
Entanglement molecular mass M_e	$g\,mol^{-1}$		2,300 2,400 (calculated)	
Tube diameter d_t	nm		430 (calculated)	
Packing length p	nm		24.3	
WLF parameters: C_1 and C_2	K	Microstructure = 96% *cis*, 2% *trans*, and 2% vinyl 1,2; reference temp. $T_0 = 29.8$°C; $T_g = 161$°C; shift factor $a_{T,S}$ of the softening dispersion	$C_1 = 3.44$ $C_2 = 196.6$	(111)
Effect of radiation: *G*-factors for cross-linking and scission, $G(x)$ and $G(s)/G(x)$	—	*Cis*-1,4	$G(x) = 5.3$ $G(s)/G(x) = 0.1$	(112, 113)
Thermal oxidative stability	K	Unspecified microstructure $T_{1/2}$ = temperature at which the polymer loses half its mass when heated in vacuum for 30 min	680	(114-117)
		T_h = upper use temperature	373	
		T_d = lowest temperature reported for thermal decomposition	598	
Biodegradability	*Cis*-1,4, $M_n = 650$; method = molecular mass measurements and biomass; inoculum = acenitobacter			—

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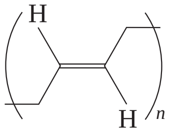
trans-1,4-Polybutadiene

ZHENGCAI PU

ACRONYMS PBD, BR

CLASS Diene elastomers

STRUCTURE



MAJOR APPLICATIONS Tire treads, carcass, belts, hoses, gaskets, seals, and protective coatings; component in other synthetic rubbers and blends.[1]

PROPERTIES OF SPECIAL INTEREST Good low-temperature properties and adhesion to metals; good resilience, durability, and abrasion resistance.[1,2,3]

PRODUCERS AND/OR SUPPLIERS Anic; Bayer; Bunawerke Huels; Bridgestone/Firestone Tire and Rubber Company; Goodyear Tire and Rubber Company; Michelin.[1]

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Anistropy of segment	cm^{-3}		$\alpha_1 - \alpha_2$	$\alpha_{\parallel} - \alpha_{\perp}$	(4)
		Benzene	$+71 \times 10^{-25}$	$+37.4 \times 10^{-25}$	
		CCl4	$+61.1 \times 10^{-25}$	$+36.3 \times 10^{-25}$	
		Cyclohexane	$+57.3 \times 10^{-25}$	$+33.1 \times 10^{-25}$	
		Toluene	$+81.6 \times 10^{-25}$	$+48.6 \times 10^{-25}$	
		p-Xylene	$+101 \times 10^{-25}$	$+60.2 \times 10^{-25}$	
Coefficient of thermal expansion	K^{-1}	Cubicle	6.75×10^{-4}		(6)
Solvents	Hydrocarbons, tetrahydrofuran, higher ketones, higher aliphatic esters				(4)
Nonsolvents	Alcohol, lower ketones and esters, nitromethane, propionitrile, water, diluted acids, diluted alkalies, hypochlorite solutions				(4)
Critical surface tension of spreading γ_c	$N\,m^{-1}$	–	0.031		(7)
Decomposition temperature	K	Initial decomposition	598		(5)
		Half decomposition; heated in vacuum for 30 min	680		
Density ρ	$g\,cm^{-3}$	–	0.93–0.97		(4)
Dielectric constant	–	1 MHz	2.51		(8)
			3.3		(6)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric loss factor	—	—	0.002	(8)
Dielectric strength	$kV\,m^{-1}$	—	400–600	(6)
Enthalpy of fusion	$J\,mol^{-1}$	Modification I Modification II	13,807 4,602	(5)
Entropy of fusion	$J\,K^{-1}\,mol^{-1}$	Modification I Modification II	26.8, 37.4 11.3, 10.9	(2, 4, 5)
Glass transition temperature	K	—	166, 171	(4, 5, 9)
Heat of fusion	$kJ\,mol^{-1}$	Modification I Modification II	4.184 4.184-4.6	(10) (11, 12)

Fractionation systems[4]

Method of fractionation	Solvent or solvent/nonsolvent mixture
Fractional precipitation	Benzene/acetone Benzene/methanol Benzene/*n*-butanol Pentane/methanol Tetrahydrofuran/water Toluene/ethanol Toluene/*n*-butanol Toluene/methanol
Fractional solution	Benzene/methanol Chloroform/methanol Ethyl ether
Fractional crystallization	Heptane
Gel permeation chromatography	Chloroform *o*-Dichlorobenzene Dichloromethane Tetrahydrofuran Toluene 1,2,4-Trichlorobenzene Trichloroethylene

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Heat capacity[4,5]

Solid		Melt	
Temperature (K)	**Heat capacity ($kJ\,K^{-1}\,mol^{-1}$)**	**Temperature (K)**	**Heat capacity ($kJ\,K^{-1}\,mol^{-1}$)**
30	0.00970	360	0.1166
40	0.01439	370	0.1184
50	0.01874	380	0.1202
60	0.02256	390	0.1220
70	0.02589	400	0.1237
80	0.02900	410	0.1255
90	0.03202	420	0.1273
100	0.03498	430	0.1291
110	0.03786	440	0.1309
120	0.04070	450	0.1326
130	0.04353	460	0.1344
140	0.04626	470	0.1362
150	0.04899	480	0.1380
160	0.05171	490	0.1390
170	0.05452	500	0.1415
180	0.05788		

Intersurface tension[4]

Surface 1	Surface 2	Interfacial tension γ_{12} ($N\,m^{-1}$)			$-d\gamma_{12}/dT$ ($N\,m^{-1}\,K^{-1}$)
		293 K	423 K	473 K	
PBD, $M_n = 960$	PDMS, $M_n = 3,900$	0.00248	0.00207	0.00191	3.22×10^{-6}
PBD, $M_n = 2,350$	PDMS, $M_n = 3,900$	0.00386	0.00270	0.00225	8.95×10^{-6}
PBD, $M_n = 960$	PDMS, $M_n = 5,200$	0.00398	0.00285	0.00242	8.65×10^{-6}
PBD, $M_n = 2,350$	PDMS, $M_n = 5,200$	0.00258	0.00225	0.00213	2.50×10^{-6}

Mark-Houwink parameters: K and a[4]

Solvent	Temperature (K)	Molecular weight ($kg\,mol^{-1}$)	K ($ml\,g^{-1}$)	*a*
Cyclohexane	313	170	0.0282	0.70
Toluene	303	160	0.0294	0.753

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength	MPa	—	14–17	(6)
Tensile modulus	MPa	—	2–10	(6)
Tensile elongation	%	—	450	(6)
Tensile compression set	%	—	10–30	(6)
Tensile resilience	%	ASTM 945	50–90	(6)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melting point	K	Modification I	370	(2, 4)
		Modification II	418	
Refractive index	–	298 K	1.515	(4)
Refractive index increment	$l\,kg^{-1}$	303 K, in cyclohexane	0.110	(4)
Scattering length density of neutron scattering	cm^{-2}	–	4.1×10^{-11}	(5)
Second virial coefficients A_2	$mol\,m^3\,kg^{-2}$ ($\times 10^{-4}$)	Solvent / Temp. (K) / M.W. ($kg\,mol^{-1}$)		(4)
		– / 307 / 17.4–370	18.3–9.48	
		Dioxane / 307 / 17.9–434	3.81–1.49	
		Toluene / 307 / 18.2–466	19.4–11.5	
Sedimentation coefficient at zero concentration $S_0(s)$	–	Diethyl ketone, 283 K		(4)
		M_w ($kg\,mol^{-1}$)		
		60	1.76×10^{-13}	
		187	2.76×10^{-13}	
		350	3.45×10^{-13}	
		436	4.28×10^{-13}	
		778	4.52×10^{-13}	
		1,380	5.15×10^{-13}	
Service temperature	K	–	172–366	(6)
Solubility parameter	$(MPa)^{1/2}$	–	14.6–17.6	(4, 5)
Theta temperature	K	Diethyl ketone	486	(5)
		Ethyl propyl ketone, $M_h = 47$–$193\,kg\,mol^{-1}$	513	
		Propylene oxide	419	
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	293 K	0.22	(5)
Transition temperature	K	Modification I to Modification II	348	(4)
Unperturbed dimension	–	328 K, in decalin		(4)
$\sigma = r_0/r_{0f}$			1.23	(4)
$C_\infty = r_0^2/nl^2$			5.8	

Surface tension[4]

M_n ($g\,mol^{-1}$)	End group	Surface tension γ ($N\,m^{-1}$)			$-d\gamma/dT$ ($N\,m^{-1}\,K^{-1}$)
		293 K	423 K	473 K	
5,400	Carboxyl acid	0.0486	0.0299	0.0227	1.440×10^{-4}
5,400	Methyl ester	0.0431	0.0288	0.0233	1.098×10^{-4}

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trans-1,4-Polybutadiene

Unit cell data[3,4]

Property	Modification I		Modification II	
Crystallographic system	PHEX	MONO	PHEX	HEX
Space group	–	C_{2h}^5	–	–
Cell dimension				
a_0 (Å)	4.54	8.63	4.88	4.95
b_0 (Å)	4.54	9.11	4.88	4.95
c_0 (Å)	4.9	4.83	4.68	4.66
α (°)	–	–	–	–
β (°)	–	114	–	–
γ (°)	–	–	–	–
Crystal density ($g\,cm^{-3}$)	1.03	1.036	0.930	0.908
Repeat distance	0.485	–	0.465	–
Repeat unit per unit cell	1	4	1	1

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Poly(butene-1)

D. R. PANSE AND PAUL J. PHILLIPS

ALTERNATIVE NAMES, ACRONYM, TRADE NAME Polybutylene, polybutene, PB, Duroflex® (Shell)

CLASS Poly{α-olefins)

STRUCTURE OF REPEAT UNIT $[-CH_2CH(C_2H_5)-]$

MAJOR APPLICATIONS Hot water and high-pressure piping; films; adhesives; comonomer for ethylene polymers; atactic polymer is used in sealants.

PROPERTIES OF SPECIAL INTEREST The polymer exhibits excellent creep properties. It is tough, retains strength at elevated temperatures, and is resistant to stress cracking and abrasion.

PREPARATIVE TECHNIQUE Ziegler-Natta polymerization: nickel-based catalysts, 80–120°C, 7–15 MPa.

Other typical catalytic systems: $TiCl_3 + Et_2AlCl$, $TiCl_3$ + cocatalyst + $MgCl_2$, chiral racemic zirconium dichloride + methylaluminoxane.[1–5]

PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Typical comonomers used	—	—	Ethylene, propylene, 1-pentene	—
Molecular weight (of repeat unit)	g mol^{-1}	—	56.11	—
Stereoregularity	—	Ziegler-Natta polymerization Catalyst system		
		1. Lithium diphenyl-phosphide + Et_2AlCl + $TiCl_3$-AA	94.7% isotactic	(6)
		2. DMH + hydrogen + Et_2AlCl + $TiCl_3$-AA	97.7% isotactic	(7)
		3. $Et_2AlCl + TiCl_3$	84.5% isotactic	(7)
Typical molecular weight range	g mol^{-1}	Ziegler-Natta polymerization		(8)
		1. Number average	7–7.5($\times 10^4$)	
		2. Weight average	7.25–7.5($\times 10^5$)	
		3. Z-average	2.5–3.0($\times 10^6$)	
Typical polydispersity index	—	Type of polymerization		
		1. Ziegler-Natta	10–11	(8)
		2. Anionic	1.02	(9)
Thermal expansion coefficient	K^{-1}	Temperature range = 140–240°C	6.7×10^{-4}	(10)

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PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Compressibility coefficient	bar^{-1}	140–240°C	10.1–15.8 ($\times 10^{-5}$)	(10)
Reducing temperature	K	None given	10,808	(11)
Reducing pressure	Pa	None given	608.5×10^{6}	(11)
Reducing volume	$cm^{-3}\ g^{-1}$	None given	1.1635	(11)
Density	$g\ cm^{-3}$	Temperature = 23°C	0.859	(12)
Solvents	–	Above 100°C	Benzene, toluene, decalin, tetralin, chloroform, chlorobenzenes	(13)
Nonsolvents	–	At room temperature	Organic solvents	(13)
Theta temperature	K	Solvent/Method used		
		1. Atactic polymer		
		Anisole/VM	356	(14)
		Anisole/PE	359.2	(15)
		Diphenyl ether/PE, VM	414	(16)
		Phenetole/VM	334	(14)
		i-Amyl acetate/PE, VM	296	(16)
		2. Isotactic polymer		
		Toluene/PE, VM	227	(16)
		Anisole/PE	362.1	(15)
		Anisole/PE, VM	362	(16)
		Cyclohexane and n-propanol (69/31 by vol.)/vm	308	(17)
		Diphenyl ether/PE, VM	421	(16)
		Phenetole/PE, VM	337.5	(16)
Polymer-solvent interaction parameter χ	–	Solvent/Temp. (°C)		(18)
		n-Heptane/115–135	0.38	
		n-Octane/115–135	0.36	
		n-Nonane/115–135	0.32	
		n-Decane/115–135	0.30	
		Benzene/135	0.49	
		Cyclohexane/135	0.20	
		2,5-Dimethylhexane/115–135	0.36	
		2,4-Dimethylpentane/115–135	0.40	
		2,3-Dimethylpentane/115–135	0.35	
		3-Ethylpentane/115–135	0.34	
		2-Methylhexane/115–135	0.39	
		3-Methylhexane/115–135	0.38	
		Toluene/135	0.47	

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PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Second virial coefficient	mol cm^3 g^{-2} ($\times 10^{-4}$)	Solvent/Temp. (°C)/Mol. wt. (10^3 g mol^{-1})		(15)
		1. Atactic polymer		
		n-Nonane/35/44.1–1,300	2.4	
		Toluene/45/26.3–558	10.8–4.1	
		2. Isotactic polymer		
		n-Nonane/80/105–935	6.05–1.05	
		Toluene/45/90.1–775	6.57–3.73	
Characteristic ratio C_∞	–	Solvent/Temp. (°C)/Method		
		Nonane/35/LS	15.1	(15)
		–/25-223/SANS	5.1–5.5	(9)
		–/5-53/VM	5.9–5.3	(6)

*PE = phase equilibria; VM = intrinsic viscosity/molar mass; LS = light scattering; SANS = small angle neutron scattering.

Mark-Houwink parameters: *K* and *a*

Solvent/method	Temp. (°C)	Mol. wt. ($\times 10^{-4}$)	$K \times 10^3$ (ml g^{-1})	*a*	Reference
Isotactic polymer					
Anisole/LS	89	57	111	0.5	(16)
Decalin/LS	115	90	9.49	0.73	(19)
Ethylcyclohexane/LS	70	94	7.34	0.80	(15)
Heptane/LS	35	90	4.73	0.80	(19)
Heptane/LS	60	90	15	0.69	(19)
Nonane/LS	80	94	5.85	0.80	(15)
Phenetole/OS*	64.5	57	113	0.5	(16)
Phenylether/OS	148	57	103	0.5	(16)
1,2,4-Trichlorobenzene/GPC	135	Not given	11.8	0.729	(20)
Cyclohexane and propanol (80/20)/LS	35	73	102	0.59	(21)
Atactic polymer					
Anisole/LS	86.2	130	123	0.5	(15)
Benzene/EG*	30	0.5	22.4	0.72	(22)
Ethylcyclohexane/LS	70	130	7.34	0.80	(15)
Phenylether/OS	141	66	104	0.5	(16)

*OS = osmotic pressure; EG = end group titration.

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Poly(butene-1)

Crystalline state properties

Crystal property	Units	Isotactic polymorphs			Reference
		I	II	III	
Lattice	—	Hexagonal	Tetragonal	Orthorhombic	(23–25)
Unit cell dimensions	Å	$a = 17.7$ $b = 17.7$ $c = 6.5$	$a = 14.85$ $b = 14.85$ $c = 20.6$	$a = 12.38$ $b = 8.92$ $c = 7.45$	(23–25)
Unit cell angles	Degree	$\alpha = \beta = \gamma = 90$	$\alpha = \beta = \gamma = 90$	$\alpha = \beta = \gamma = 90$	(23–25)
Monomer per unit cell	—	18	44	8	(23–25)
Helix conformation	—	31	113	41	(23–25)
Space group	—	D3D-6	Not given	Not given	(23)
Crystalline density at 23°C	g cm^{-3}	0.951	0.902	0.905	(23–25)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Degree of crystallinity	%	Form I obtained after extrusion	48–55	(8)
Heat of fusion	kJ mol^{-1}	—	6.318	(26, 27)
		—	6.276	(26, 27)
		—	6.485	(26, 27)
		Clapeyron equation	7.782	(28, 29)
			7.531	(28, 29)
Entropy of fusion	kJ K^{-1} mol^{-1} ($\times 10^{-3}$)	—	15.5	(26, 27)
		—	15.8	(26, 27)
		Clapeyron equation	19.2	(28, 29)
Avrami exponent	—	Compression molded, cooled at 40°C min^{-1} from 180°C	0.9–1.07	(30)
		Blown film samples, draw ratio between 1 and 6	0.32–0.74	
Glass transition temperature	K	Method employed = DMA	256–248	(31)
Melting point	K	1. Isotactic polymer		(13)
		I	411–415	
		II	393–403	
		III	374–383	
		2. Syndiotactic polymer		
		I	323	
		II	323	
Sub-T_g transition temperatures	K	Nature of transition: onset of local motion of side groups	115	(31)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat capacity	$kJ\ K^{-1}\ mol^{-1}$	Temperature (K)		(32)
		100	0.0377	
		200	0.0684	
		300	0.1170	
		600	0.1720	
Polymers with which compatible	–	All proportions	PP	(33)
Tensile modulus	MPa	ASTM D638	290–295	(8)
Tensile strength at yield	MPa	ASTM D638	16–18	(8)
Tensile strength at break	MPa	ASTM D638	32–35	(8)
Elongation at break	%	ASTM D638	275–320	(8)
Flexural modulus	MPa	ASTM D790	375–380	(8)
Notched Izod impact strength	$J\ m^{-1}$	ASTM D256	640–800	(8)
Hardness, Shore D	–	ASTM D2240	55–65	(8)
Poisson ratio	–	At 25°C	0.47	(34)
Dart impact strength	g	ASTM D1709 (for film thickness = 50.8 μm)	350	(8)
Elmendorf tear strength	$kN\ m^{-1}$	ASTM D1922 (for film thickness = 50.8 μm)		(8)
		MD	425	
		TD	386	
Index of refraction *n*	–	Isotactic polymer	1.5125	(8)
Birefringence	–	Polymorphs		(35)
		I	0.034	
		II	0.013	
Refractive index increment dn/dc	$ml\ g^{-1}$	Solvent/Temperature (°C)		
		n-Nonane/35	0.092	–
		n-Nonane/80	0.108	–
		1-Chloronaphthalene/135	−0.206	(36)
		Cyclohexane/25	0.074	(37)
Dielectric constant	–	103–106 Hz	2.53	(8)
Dissipation factor	–	103–106 Hz	0.0005	(8)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Thermal conductivity	$W m^{-1} K^{-1}$	ASTM C177	0.22	(8)
Melt index	$g (10 min)^{-1}$	ASTM D 1238 (E)	0.4	(8)
Oxygen permeability	m^3 (STP)m s^{-1} m^{-2} Pa^{-1}	Film thickness = 100 mil	1.74×10^{-15}	(38)
Heat-deflection temperature	K	At 1.82 MPa, ASTM D648 At 0.46 MPa, ASTM D648	327–333 375–386	(8)
Brittleness temperature	K	ASTM D746	255	(8)
Water absorption	%	24 h, ASTM D570	<0.03	(8)

Suppliers: Shell Chemical Company, USA (27,000 tons/yr)
Mitsui Petrochemicals, Japan
Neste Oy and Idemitsu, Finland

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Poly[(*n*-butylamino)thionyl-phosphazene]

IAN MANNERS

CLASS Inorganic and semi-inorganic polymers

STRUCTURE $[NSO(HN^{n}Bu)\{NP(NH^{n}Bu)_2\}_2]_n$

PROPERTIES OF SPECIAL INTEREST Low cost, ease of synthesis, high gas permeability and low glass transition temperature.

SYNTHESIS Poly[(*n*-butylamino)thionylphosphazene] can be prepared via the aminolysis of the chlorinated poly(thionylphosphazene) with butylamine.(1) The chlorinated poly(thionylphosphazene) is synthesized via the thermal ring opening polymeriztion (ROP) of the corresponding cyclic thionylphosphazene $[SOCl(NPCl_2)_2]$.(1)

PROPERTY	UNITS	CONDITION	VALUE	REFERENCE
Glass transition temperature	K	DSC experiment	257	(1)
Unit cell dimensions		For monomer $[SOCl(NPCl_2)_2]$		(2)
Lattice	–	–	Orthorhombic	–
Monomers per unit cell	–	–	4	–
Cell dimensions	Å	–	$a = 7.461$	–
			$b = 8.359$	–
			$c = 16.228$	–
Cell angles	Degrees	–	$\alpha = \beta = \gamma = 90$	–

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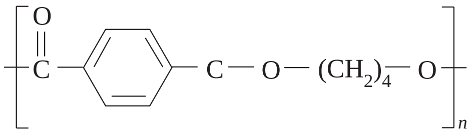
Poly(butylene terephthalate)

JUDE O. IROH

ACRONYM PBT

CLASS Polyesters; linear and flexible aromatic polyesters; thermoplastics

STRUCTURE



MAJOR APPLICATIONS Molding plastic, molecular component of polyether ester thermoplastic block copolymer elastomer, fiber and plastic forming, used in tooth and paint brush and in bristles and filler fabrics.

PROPERTIES OF SPECIAL INTEREST Mostly synthesized as flexible semicrystalline thermoplastic, PBT has outstanding resilience and toughness. High toughness and resilience is due to improved chain flexibility derived from the four methylene units. Used in thermoplastic matrix composites for gears, machine parts, small pump housings, and insulators.

PREPARATIVE TECHNIQUES Synthesized by step-growth polymerization between butylene glycol and terephthalic acid. PBT is often synthesized by ester-exchange polymerization using weak basic catalysts such as alkanoates, hydrides, and alkoxides of sodium, lithium, zinc, calcium, magnesium, titanium, etc. PBT is formed by the reaction of dimethyl terephthalate with 1,4-butanediol at 0.020 atm and 160–230°C. Final reaction occur at 260–300°C under vacuum at 0.001 atm.[(1–4)]

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Molecular conformation	—	—	Nearly planar		—
Unit cell	—	—	Triclinic/allomorphs		(4)
Lattice constants	degrees	X-ray diffraction	α	β	(5, 6)
		a	4.86	4.72	
		b	5.96	5.79	
		c	1.165	1.300	
		α	99.70	102.70	
		β	116	120.2	
		γ	110.8	103.7	
Unit cell volume	nm^3	X-ray diffraction	$\alpha = 0.2615$, $\beta = 0.2729$		(5, 6)
Number of chains per unit cell	—	—	1		(6)
Unit cell density	$g\,cm^{-3}$	X-ray diffraction	$\alpha = 1.397$, $\beta = 1.338$		(6)

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Poly(butylene terephthalate)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Measured density	g cm^{-3}	–	$\alpha = 1.34$, $\beta = 1.33$	(6)
Number of chains	–	–	1	(5, 6)
Number of monomers	–	–	1	(5, 6)
Glass transition temperature T_g	K	ASTM D3418	303–333	(5, 7, 8)
Melting temperature T_m	K	ASTM D3418	495–505	(3, 5, 8, 9)
Heat of fusion ΔH	kJ mol^{-1}	DSC	21.2	(5, 7)
Breaking strength σ_B	MPa	ASTM D638	55	(5, 8, 10–14)
Tensile (Young's) modulus E	MPa	ASTM D638	2,600	(5, 8, 10–14)
Flexural modulus (rigidity) E	MPa	3-point flexure, ASTM D790	2,300	(5, 8, 10–14)
Ultimate strain ε_B	%	ASTM D638	200–300	(5, 8, 10–14)
Yield strain ε_Y	%	ASTM D638	4	(5, 8, 10–14)
Yield strength σ_Y	MPa	ASTM D638	52	(15)
Impact strength	J m^{-1}	ASTM D256-86	53	(5, 8, 10–14)
Linear coefficient of thermal expansion α	K^{-1}	ASTM D696	7.0×10^{-5}	(5, 8, 13–15)
Specific heat	kJ kg^{-1} K^{-1}	–	223	(5, 8, 13, 14)
Thermal conductivity	W m^{-1} K^{-1}	–	1.35	(5, 8, 13, 14)
Thermal deflection	K	ASTM D648		(5, 8, 13, 14)
		At 264 psi	54	
		At 66 psi	154	
Outdoor weathering	%	ASTM D1435	Good resistance	(5, 8, 13, 14)
Volume resistivity	ohm cm ($\times 10^{16}$)	ASTM D257	0.1	(5, 8, 13, 14)
Dissipation factor	100 Hz	D150	0.005	(5, 8, 13, 14)
	106 Hz	D150	0.012	
Dielectric strength	kV mm^{-1}	ASTM D149	15.8	(5, 8, 13, 14)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric constant	10^6 Hz	ASTM D150	3.24	(5, 8, 13, 14)
Mark-Houwink parameters: K and a	$K = \text{ml g}^{-1}$ a = None	Solution viscometry (30°C)	$K = 1.17 \times 10^{-2}$ $a = 0.87$	(5, 16)
Molecular weight (of repeat unit)	g mol^{-1}	–	220	–
Weight average molecular weight	g mol^{-1}	Light scattering	30,000–80,000	(5, 17)

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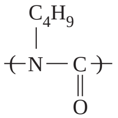
Poly(*n*-butyl isocyanate)

CHANDIMA KUMUDINIE AND JAGATH K. PREMACHANDRA

ACRONYM PBIC

CLASS Poly(isocyanates); N-substituted 1-nylons

STRUCTURE



MAJOR APPLICATION An ideal example of a polymer model for a rigid-rod macromolecular chain material amenable to physical studies.

PROPERTIES OF SPECIAL INTEREST Hydrodynamic rigid-rod molecule, unusual chain stiffness, helical conformation.[1]

OTHER POLYMERS SHOWING THIS SPECIAL PROPERTY Rigid-rod molecule, helical conformation: poly(*n*-hexyl isocyanate), poly(γ-benzyl-L-glutamate).

Preparative techniques

Polymerization process	Solvent	Temp. (°C)	Catalyst	Reference
Anionic	Benzene	−55	NaCN in dimethylformamide	(2)
Anionic	Toluene-THF	–	*n*-Butyllithium	(3)
Anionic	Toluene	−78	*n*-Butyllithium	(4)
Anionic	Toluene	−78	Fluorenyl sodium	(4)
Anionic	Toluene	−78	Ethyllithium in benzene	(5)
Anionic	Toluene	−78	$(C_2H_5)_2Be$	(5)
Anionic	–	−40 to −70	NaCN in dimethylformamide	(6)
Anionic	CH_2Cl_2	−78	*n*-Octyl sodium	(5)
Anionic	$CS_2$2	−78	Ethyllithium in benzene	(5)
Anionic	THF	−78	Ethyllithium in benzene	(5)
Anionic	Acetone	−78	$LiOC_4H_9$	(5)
Anionic	CH_2Cl_2	−78	Ethyllithium in benzene	(5)
Cationic*	–	–	–	(5)

*No polymers were obtained.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight of repeat unit	$g\,mol^{-1}$	–	99	–
Typical molecular weight range of polymer	$g\,mol^{-1}$	M_w	$(0.14–2.3) \times 10^6$	(1)
		M_w	$(1.75–2.4) \times 10^5$	(7)
		M_w	$(0.23–5.3) \times 10^5$	(8)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Typical polydispersity index (M_w/M_n)	–	–	1.0–1.2	(9)
		–	2.5	(9)
		–	1.07–1.20	(10)
		Light scattering and osmometry	1.15–1.30	(11)
		Dielectric measurements	1.06–1.44	(11)
		In chloroform, initiator: NaCN in dimethylformamide	1.1–1.4	(4)
		In chloroform, initiator: fluorenyl sodium	1.1–9.5	(4)
		In chloroform, initiator: *n*-butyllithium	1.3–8.4	(4)
		In benzene, dielectric measurements	3.2–4.4	(4)
IR (characterisitc absorption frequencies)	cm^{-1}	Carbonyl, solid state	~1,700	(2, 5, 12–14)
		Carbonyl, dilute solution	1,690–1,695	(13, 14)
		Disubstituted amide, solid state	1,282 and 1,390	(2)
UV	nm	Absorption maxima at the high wavelength band, λ_{max}	254	(15, 16)
	$L\,mol^{-1}\,cm^{-1}$	Extinction coefficient	3.7×10^3	(16)
NMR	^{13}C NMR, 125.7-MHz spectrometer, in $CDCl_3$ at 55°C			(16)
	^{13}C NMR, , 20-MHz spectrometer			(13, 17)
	^1H NMR, poly[(S)-(+)-2-methylbutyl isocyanate], 220-MHz spectrometer			(18)
	^1H NMR			(13, 17)
Solvents	Aromatic and chlorinated hydrocarbons			(2)
	Nonpolar solvents such as benzene and toluene			(1)
	THF, benzene, toluene			(3, 7)
	CCl_4, $CHCl_3$, 1,2,4-trichlorobenzene-chloroform (75/25 v/v)			(7)
Nonsolvents	Methanol			(2, 19)
	Acetone, ethyl acetate, dimethylformamide, methylethylketone			(3)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Second virial coefficient	$mol\,cm^3\,g^{-2}$	In toluene at 37°C, $M_n = (0.23\text{–}5.3) \times 10^5\ g\,mol^{-1}$, osmometry	$(1.85\text{–}2.36) \times 10^{-3}$	(8)
		In toluene at 37°C, $M_n = (0.23\text{–}5.2) \times 10^5\ g\,mol^{-1}$, osmometry	$(1.8\text{–}2.5) \times 10^{-3}$	(4)
		In toluene, osmometry, arithmetic mean	2.13×10^{-3}	(4)
		In chloroform, $M_w = 6.1 \times 10^4\ g\,mol^{-1}$	3×10^{-3}	(4)
		In chloroform, $M_w = 1.0 \times 10^7\ g\,mol^{-1}$	2.1×10^{-3}	(4)
		In chloroform, $M_w = 1.03 \times 10^5\ g\,mol^{-1}$	1.5×10^{-3}	(4)
		In chloroform, $M_w = 5.40 \times 10^5\ g\,mol^{-1}$	2.5×10^{-3}	(4)
		In chloroform, $M_w = 1.65 \times 10^5\ g\,mol^{-1}$	2.0×10^{-3}	(4)
		In chloroform, $M_w = 2.45 \times 10^6\ g\,mol^{-1}$	2.4×10^{-3}	(4)
		In chloroform, light scattering, arithmetic mean	2.51×10^{-3}	(4)
Mark–Houwink parameters: *K* and *a*	–	In tetrahydrofuran	$a = 1.18$	(20)
	–	In carbon tetrachloride	$K = 3.16 \times 10^{-4}$, $a = 1.2$	(21, 22)
Huggins constant	–	In carbon tetrachloride at 22°C	0.27–0.97	(10)
Radius of gyration	Å	In chloroform, $M_w = 6.1 \times 10^4\ g\,mol^{-1}$	320	(4)
		In chloroform, $M_w = 1.0 \times 10^7\ g\,mol^{-1}$	5,200	
		In chloroform, $M_w = 1.03 \times 10^5\ g\,mol^{-1}$	420	
		In chloroform, $M_w = 5.40 \times 10^5\ g\,mol^{-1}$	1,250	
		In chloroform, $M_w = 1.65 \times 10^5\ g\,mol^{-1}$	625	
		In chloroform, $M_w = 2.45 \times 10^6\ g\,mol^{-1}$	2,800	
Monomer projection length	Å	Translation diffusion	2.0	(21)
		Rotatory diffusion	2.7	(21)
		Viscosity	2.0	(21)
		Viscosity	1.50–1.80	(10)
		Relaxation time measurements	1.19–1.49	(10)
		Viscosity sedimentation-diffusion	2.1	(23, 24)
		Dielectric measurements	1.1	(25)
		Dielectric and viscoelastic relaxation	0.6–1.1	(26)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Monomer projection length	Å	In chloroform, light scattering	1.8–2.1	(4, 27)
		In chloroform	2	(28)
		X-ray diffraction	1.94	(29)
Chain diameter	Å	In toluene at 37°C, osmometry	10	(27)
			11	(9)
Number of monomer units in segment of molecular chain	–	Translatory diffusion	600	(21)
		Rotatory diffusion	500	
		Flow birefringence	370	
		Birefringence in an electric field	700	
Persistence length	Å	In carbon tetrachloride	600	(21)
		In chloroform	500–600	(27)
		In chloroform	300	(28)
		Viscosity sedimentation-diffusion	1,300	(23, 24)
		Dielectric measurements	880	(25)
		Dielectric and viscoelastic relaxation	>400	(26)
		Light scattering	500–600	(4)
Space group	Triclinic with the axes of the molecule at 1/3, 1/6, *z* and 2/3, 5/6, *z*			(29)
Chain conformation	Rigid rod, nonpolar, and possibly helical			(1)
	Helical structure with a translation of 1.94 Å and a rotation of 135° per monomeric unit (8_3 helix)			(29)
	Rigid rod up to degree of polymerization, DP ~ 600, with an onset of flexibility at higher DP			(30)
	The conformation of the polymer is same in the solid phase and in solution			(29)
	The onset of flexibility occurs at $M_w = (0.73–1.33) \times 10^5$ g mol^{-1}			(15)
	Flexibility is encountered when $M_w > 5.0 \times 10^4$ g mol^{-1}			(9)
	Low molecular weight molecule, $M_w < 8.0 \times 10^4$ is rodlike and helical. At high molecular weight, $M_w > 1.0 \times 10^6$, the polymer chain conformation is random coil			(25)
Unit cell dimensions				(29)
Lattice	–	–	Pseudohexagonal	
Monomers per unit cell	–	–	2	
Cell dimensions	Å	–	$a = b = 13.3$, $c = 15.4$	
Degree of crystallinity	%	$[\eta] = 4.2$ dl g^{-1} in benzene	44.5	(5)
		$[\eta] = 7.3$ dl g^{-1} in benzene	36.4	(5)
		$[\eta] = 10.6$ dl g^{-1} in benzene	22.7	(5)
		$[\eta] = 11.6$ dl g^{-1} in benzene	19.1	(5)
		Relatively high and depends on the catalyst used in polymerization	–	(5)
		Depends on the post treatment of the polymer	–	(31)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Degree of crystallinity	%	Higher degree of crystallinity of the polymer prepared with C_2H_5Li than with NaCN in dimethylformamide	–	(5)
Density	$g\,cm^{-3}$	–	0.97	(29)
		–	1.25	(7)
		Highly crystalline	1.071	(25)
		Calculated	1.10	(29)
Glass transition temperature	K	DSC	None observed	(7)
		DTA-DSC, at 20°C min^{-1}; Ar atmosphere	258	(13)
Melting point	K	DTA-DSC; Ar atmosphere; heating rate: 20°C min^{-1}	~458	(13)
		^{13}C NMR thermal cycling in the bulk	463	(17)
		Polymerization catalyst: *n*-octyl sodium; solvent: CH_2Cl_2	438	(5)
		Polymerization catalyst: C_2H_5Li in benzene; solvent: THF	438	(5)
		By hot-stage microscopy	487	(32)
			471–473	(31)
			472–474	(31)
			482	(33)
Mesomeric transition temperatures	K	Crystalline-nematic transition, by hot-stage microscopy	484	(32)
Sub-T_g transition temperatures	K	Relaxations, by hot-stage microscopy	444	(32)
Softening temperature	K	–	453	(2, 33)
Enthalpy of propagation	$kJ\,mol^{-1}$	–	5.7	(6)
Tensile modulus	MPa	At room temperature, η_{sp}/C in $CHCl_3 = 8.1\,dl\,g^{-1}$	~810	(13)
		At 23°C, strain rate $= 8.3 \times 10^{-4}\,s^{-1}$	~500	(34)
		At 20°C, strain rate $= 6.7 \times 10^{-4}\,s^{-1}$	~1,570	(7)
		At 80°C, strain rate $= 6.7 \times 10^{-4}\,s^{-1}$	~2,940	(7)
		At 0°C, strain rate $= 6.7 \times 10^{-4}\,s^{-1}$	~1,765	(7)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength	MPa	At room temperature, η_{sp}/C in $CHCl_3 = 8.1\,dl\,g^{-1}$	~45	(13)
		At 23°C, strain rate $= 8.3 \times 10^{-4}\,s^{-1}$	~52	(34)
		At −20°C, strain rate $= 6.7 \times 10^{-4}\,s^{-1}$, 30–40% crystalline, $\eta = 7.25\,dl\,g^{-1}$	~58	(7, 35)
		At 0°C, strain rate $= 6.7 \times 10^{-4}\,s^{-1}$, 30–40% crystalline, $\eta = 7.25\,dl\,g^{-1}$	~50	(7, 35)
		At 23°C, strain rate $= 6.7 \times 10^{-4}\,s^{-1}$, 30–40% crystalline, $\eta = 7.25\,dl\,g^{-1}$	~34	(7, 35)
Maximum extensibility	%	At room temperature, η_{sp}/C in $CHCl_3 = 8.1\,dl\,g^{-1}$	32	(13)
		At 23°C, strain rate $= 8.3 \times 10^{-4}\,s^{-1}$	~33	(34)
		At −20°C, strain rate $= 6.7 \times 10^{-4}\,s^{-1}$, 30–40% crystalline, $\eta = 7.25\,dl\,g^{-1}$	~15	(7, 35)
		At 0°C, strain rate $= 6.7 \times 10^{-4}\,s^{-1}$, 30–40% crystalline, $\eta = 7.25\,dl\,g^{-1}$	~23.5	(7, 35)
		At 23°C, strain rate $= 6.7 \times 10^{-4}\,s^{-1}$, 30–40% crystalline, $\eta = 7.25\,dl\,g^{-1}$	~39	(7, 35)
Specific refractive index increment, dn/dc	$ml\,g^{-1}$	In chloroform, $\lambda_0 = 5{,}460$ Å	0.054	(1, 11)
		In tetrahydrofuran, $\lambda_0 = 4{,}358$ Å	0.99	(27)
Relative electrical birefringence	—	In carbon tetrachloride, frequency $< 5 \times 10^3$ Hz, $M_w = 2.46 \times 10^5\,g\,mol^{-1}$	~1–0.03	(21)
		In carbon tetrachloride; frequency range: 10^3–10^4 Hz; $M_w = 2.0 \times 10^4\,g\,mol^{-1}$	~1–0.75	
Dielectric constant ε'	—	In dilute benzene solution ($10^{-4}\,g\,cm^{-3}$), at 22.5°C; frequency range: 10^{-1} to 2×10^6 Hz; $M_w = 1.84 \times 10^6\,g\,mol^{-1}$	~2.28–2.76	(1)
		In carbon tetrachloride at 22.9°C; frequency range: 10^{-1}–10^6 Hz; $M_w = 2.35 \times 10^5\,g\,mol^{-1}$	2.35–2.37	(25)
Dielectric loss ε''	—	In dilute benzene solution ($10^{-4}\,g\,cm^{-3}$), at 22.5°C; frequency range: 10^{-1} to 2×10^6 Hz; $M_w = 1.84 \times 10^6\,g\,mol^{-1}$	~0.01–0.10	(1)
		In carbon tetrachloride at 22.9°C; frequency range: 10^{-1}–10^6 Hz; $M_w = 2.35 \times 10^5\,g\,mol^{-1}$	~0.003–0.053	(11, 25)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric critical frequency	Hz	In dilute benzene solution (10^{-4} g cm^{-3}), at 22.5°C; frequency range: 10^{-1} to 2×10^6 Hz; $M_w = (0.14$–$2.3) \times 10^6$ g mol^{-1}	100,000–32	(1)
		In carbon tetrachloride at 22.9°C; frequency range: 10^{-1}–10^6 Hz; $M_w = 2.35 \times 10^5$ g mol^{-1}	~540	(11, 25)
Relaxation time	μs	In dilute benzene solution (10^{-4} g cm^{-3}), at 22.5°C; frequency range: 10^{-1} to 2×10^6; $M_w = (0.14$–$2.3) \times 10^6$ g mol^{-1}	1.6–5,000	(1)
		In tetrahydrofuran, $M_w = 3 \times 10^5$ g mol^{-1}	17.8	(9)
		In chloroform, $M_w = 3 \times 10^5$ g mol^{-1}	20.0	(9)
		In benzene, $M_w = 3 \times 10^5$ g mol^{-1}	25.0	(9)
		In benzene, $M_w = 1.33 \times 10^5$ g mol^{-1}	30.0	(9)
		In benzene, $M_w = 6.0 \times 10^4$ g mol^{-1}	3.3	(9)
		In benzene, $M_w = 2.0 \times 10^4$ g mol^{-1}	0.42	(9)
		In carbon tetrachloride at 22°C, $M_w = (0.2$–$3.8) \times 10^5$ g mol^{-1}	0.40–1,260	(10)
		In carbon tetrachloride at 22.9°C, $M_w = (2$–$7.3) \times 10^4$ g mol^{-1}	~0.40–20	(25)
		In carbon tetrachloride at 22.9°C, $M_w = (1.03$–$5.4) \times 10^5$ g mol^{-1}	~45–1,995	(25)
		In carbon tetrachloride at 22.9°C, $M_w = (0.12$–$1.0) \times 10^7$ g mol^{-1}	~4,467–89,125	(25)
Dipole moment *D*	–	Net dipole moment is parallel to the major axis of the molecule		(1)
		$M_w = 1.7 \times 10^6$ g mol^{-1}	4,500	(36)
		$M_w = 3.8 \times 10^5$ g mol^{-1}	2,120	(36)
		In benzene, $M_n = 1.2 \times 10^5$ g mol^{-1}, specific volume = 0.8 cm^{3}g^{-1}	1,224	(9)
		In benzene, $M_n = 5 \times 10^4$ g mol^{-1}, specific volume = 0.8 cm^{3}g^{-1}	481	(9)
		In benzene, $M_n = 2 \times 10^4$ g mol^{-1}, specific volume = 0.8 cm^{3}g^{-1}	179	(9)
		In carbon tetrachloride at 22.9°C, $M_w = (2$–$7.3) \times 10^4$ g mol^{-1}	226–726	(25)
		In carbon tetrachloride at 22.9°C, $M_w = (1.03$–$5.4) \times 10^5$ g mol^{-1}	806–2,561	(25)
		In carbon tetrachloride at 22.9°C, $M_w = (1.2$–$3.5) \times 10^6$ g mol^{-1}	3,768–6,277	(25)
		In carbon tetrachloride at 22.9°C, $M_w = (0.54$–$1.0) \times 10^7$ g mol^{-1}	2,561–10,954	(25)
Anisotropy of the monomer unit	–	–	1.1×10^{-24}	(21)
			1.46×10^{-24}	(37)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Anisotropy of the Kuhn statistical segment	—	—	3.6×10^{-22}	(21)
Kerr constant	—	—	$(0.25–24) \times 10^{-7}$	(21)
Optical activity $[\alpha]_D$	Degree	Poly[(S)-(+)-2-methylbutyl isocyanate], in chloroform	+160	(18)
Reduced dichorism	—	In carbon tetrachloride at 22.9°C, $M_w = 73{,}000\ g\ mol^{-1}$, field strength $\sim(1.3–2.3) \times 10^4\ V\ cm^{-1}$	~0.24–0.068	(15)
Diffusion coefficient D	—	In carbon tetrachloride, $M_w = 10^3–10^6\ g\ mol^{-1}$	$(0.075–1.6) \times 10^{-6}$	(21)
		$M = (0.10–3.0) \times 10^5\ g\ mol^{-1}$	$1.07 \times 10^{-3}\ M^{-0.8}$	
Rotatory diffusion coefficient	S^{-1}	In tetrahydrofuran, $M_w = 3.0 \times 10^5\ g\ mol^{-1}$	2.8×10^4	(9)
		In chloroform, $M_w = 3.0 \times 10^5\ g\ mol^{-1}$	2.5×10^4	
		In benzene, $M_w = 3.0 \times 10^5\ g\ mol^{-1}$	2.0×10^4	
		In benzene, $M_w = 1.33 \times 10^5\ g\ mol^{-1}$	1.66×10^4	
		In benzene, $M_w = 6.0 \times 10^4\ g\ mol^{-1}$	1.5×10^5	
		In benzene, $M_w = 2.0 \times 10^4\ g\ mol^{-1}$	1.20×10^6	
Index of sedimentation $[S]$	—	In carbon tetrachloride, $M_w = 10^3–10^6\ g\ mol^{-1}$	$\sim(1.26–1.38) \times 10^{-13}$	(21)
		$M = (0.10–3.0) \times 10^5\ g\ mol^{-1}$	$1.97 \times 10^{-14}\ M^{0.2}$	
Intrinsic viscosity $[\eta]$	$dl\ g^{-1}$	In benzene, $C = 0.2\ g\ dl^{-1}$	1.2	(31)
		In carbon tetrachloride, $10^3–10^6\ g\ mol^{-1}$	~12–2,370	(21)
		$M = (0.10–3.0) \times 10^5\ g\ mol^{-1}$	$3.16 \times 10^{-4}\ M^{1.2}$	(21)
Decomposition temperature	K	At polymer melting point	482	(2)
		TGA, heating rate: $10°C\ min^{-1}$	~423	(13)
		TGA, heating rate: $20°C\ min^{-1}$, nitrogen atmosphere	458	(38)
		By hot-stage microscopy	~492	(32)

Pyrolyzability[38]

	Conditions	Observation
Nature of product	Direct pyrolysis mass spectrometry	Cyclic trimer of *n*-butyl isocyanate as the principle decomposition product, and trace amounts of monomer

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Poly(ε-caprolactone)

JUDE O. IROH

ACRONYM PCL

CLASS Polyesters; linear aliphatic flexible polyesters; thermoplastics

STRUCTURE

$$\left[\overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_5 - O \right]_n$$

MAJOR APPLICATIONS Films, formulation of copolymers, biodegradable polyesters, formulation of elastomeric block copolyesters, formation of diol for extension by diisocyanate.

PROPERTIES OF SPECIAL INTEREST Mostly synthesized as semicrystalline thermoplastic. PCL is a clear and flexible polyester with elastomeric properties.

PREPARATIVE TECHNIQUES Synthesized by ring-opening addition polymerization of ε-caprolactone at 170°C in a nitrogen atmosphere using dibutyl stanneous oxide (Bu_2SnO) as the catalyst. A wide range of initiators such as organometal catalysts and alkanolamine can be used.[1–7] The copolymer poly(ε-caprolactone-co-ethylene glycol) is used as a diol extension for polyurethane.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular conformation	—	—	Nearly planar	—
Molecular weight (of repeat unit)	$g\ mol^{-1}$	—	114	—
Weight average molecular weight	$g\ mol^{-1}$	GPC	74,000	(8)
Number average molecular weight	$g\ mol^{-1}$	GPC	25,000	(11)
Intrinsic viscosity	$cm^3\ g^{-1}$	Dilute solution viscometry	0.9	(10)
Solvents	—	—	Dimethylacetamide(DMAc), benzene, chloroform	(9, 13)
Enthalpy of polymerization	$kJ\ mol^{-1}$	25°C and 1 atm	−28.8	(8)
Entropy of polymerization	$kJ\ mol^{-1}$	25°C and 1 atm	−53.9	(8)
Gibbs free energy of polymerization	$kJ\ mol^{-1}$	25°C and 1 atm	−12.8	(8)

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Poly(ε-caprolactone)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Physical state	–	Semicrystalline	–	–
Degree of crystallinity	%	DSC	69	(11)
Unit cell	–	– X-ray diffraction	Orthorhombic: 2θ peaks at 22° and 24°	(9–12)
Lattice constants	Å	X-ray diffraction	a = 7.45 $b = 4.98$ $c = 17.05$	(10)
Number of repeat units per unit cell	–	–	4	(10)
Unit cell density	g cm^{-3}	X-ray diffraction	1.20	(10)
Measured density	g cm^{-3}	X-ray diffraction	1.094–1.2000	(8, 10, 12)
Elongation	%	–	700	(8)
Glass transition temperature T_g	K	DSC	201	(8, 12)
Melting temperature T_m	K	DSC	331	(8, 12)
Heat of fusion ΔH_f	kJ mol^{-1}	DSC	8.9	(12)

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Polycarbonate

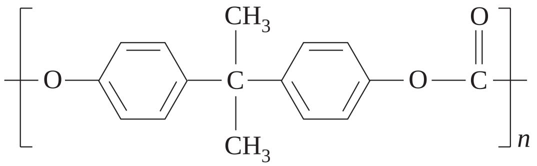
TAREK M. MADKOUR

ACRONYM, ALTERNATIVE NAME, TRADE NAMES PC, bisphenol-A polycarbonate, Lexan® (GE), Makrolon® (Bayer)

CLASS Polyesters

SYNTHESIS Polycondensation

STRUCTURE



MAJOR APPLICATIONS Used in making canopies for supersonic aircraft, bubble helmets for astronauts, break-resistant windows, and bullet-resistant laminates for banks and armored cars. It is also used for computer housings where mechanical, electrical and fire-resistance properties are needed. It is also used in steam-sterilizable food-processing equipment.

PROPERTIES OF SPECIAL INTEREST Polycarbonate engineering thermoplastics are amorphous, clear polymers that exhibit superior dimensional stability, good electrical properties, good thermal stability, and outstanding impact strength. They also offer excellent moldability and extrudability, low-temperature toughness, and the availability of flame-retardant and other special grades.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	254	(1)
Typical molecular weight (M_n)	$g\,mol^{-1}$	–	11,000	(1)
Typical polydispersity index (M_w/M_n)	–	–	2.7	(1)
Infrared bands (frequency)	cm^{-1}	Assignment		(2)
		Para out-of-plane aromatic CH wag, two adjacent Hs	830	
		Para in-plane aromatic CH bend	1,015	
		$(CH_3)_2$ rock/C–C stretch	1,080	
		Carbonate C–O stretch	1,160	
		Carbonate C–O stretch	1,193	
		Carbonate aryl-O-aryl C–O stretch	1,230	
		CH_3 symmetric (umbrella) deformation	1,362	
		Para aromatic ring semicircle stretch	1,405	

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Infrared bands (frequency)	cm^{-1}	Assignment			(2)
		Para aromatic ring semicircle stretch		1,505	
		Para aromatic ring quadrant stretch		1,600	
		Carbonate C=O stretch		1,775	
		CH_3 symmetric stretch		2,875	
		CH_3 asymmetric stretch		2,970	
		Aromatic CH stretches		3,000–3,200	
UV absorption cut-off	cm	—		280×10^7	(3)
Raman frequencies	cm^{-1}	Assignment	Motion		(4)
		Phenyl ring	Diagonal breathing	634	
		Phenyl ring	Breathing	702	
		Phenyl ring	Breathing	732	
		Methyl group	Bond stretching	885	
		Phenyl ring	Lateral stretching	1,108	
		Phenyl ring	Lateral stretching	1,177	
		Carbonyl	Stretching	1,232	
		Quaternary carbon	Bond stretching	1,600	
Thermal expansion coefficient	K^{-1}	Measured at 40°C		2.6×10^4	(5)
Isothermal compressibility	bar^{-1}	Measured at 40°C and atmospheric pressure		2.6×10^5	(5)

Tait equation parameters[3]

	C	B_0 (bar)	b_1 (°C^{-1})
Below T_g	0.0894	3,878	0.00261
Above T_g	0.0894	3,100	0.00408

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	ASTM D792	1.2	(1)
Solvent/nonsolvent mixtures	—	Temperature		
		23°C	Chloroform/methanol	(6)
		50°C	Chloroform/*n*-octane	
		−20°C	Methylene chloride-cresol/petroleum ether	
Theta temperature	K	*n*-Butyl benzyl ether	443	(7)
		Dioxane/cyclohexane (64/36)	298	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Second virial coefficient	mol cm^3 g^{-2}	THF at 25°C for mol. wt. = 76.9–31.6 ($\times 10^3$) g mol^{-1}	11.0–13.0 ($\times 10^4$)	(8)
Intrinsic viscosity	dl g^{-1}	Chloroform at 30°C	0.5–0.55	(1)
Mark-Houwink parameters: K and a	K = ml g^{-1} a = None	n-Butyl benzyl ether at 170°C, for mol. wt. = 4.0×10^4 g mol^{-1}	$K = 210 \times 10^3$ $a = 0.50$	(7)
Characteristic ratio C_∞	–	Calculated for very high molecular weights	2.4	(9)
Glass transition temperature	K	Dielectric measurements at frequency of 10 Hz	423	(3)
Sub-T_g transition temperature	K	β-relaxation temperature γ-relaxation temperature	343 173	(3)
Heat capacity	kJ K^{-1} mol^{-1}	–	0.32	(1)
Heat deflection temperature	K	At 1.82 MPa	405	(1)
Vicat softening point	K	–	430	(3)
Tensile modulus	MPa	ASTM: D638, D759, D1708	2,380	(1, 3)
Tensile strength	MPa	At yield At ultimate	62.1 65.5	(1)
Yield strain $(L/L_0)_y$	%	–	6–8	(1)
Maximum extensibility $(L/L_0)_r$	%	–	110	(1)
Flexural modulus	MPa	–	2,340	(1)
Flexural strength	MPa	–	93.1	(1)
Impact strength	J m^{-1}	Izod, notched	850	(3)
Entanglement molecular weight	g mol^{-1}	–	4,800	(9)
WLF parameters: C_1 and C_2	–	$T_0 = 418$ K	$C_1 = 22.88$ $C_2 = 78.64$	(3)
Index of refraction	–	Measured at room temperature	1.586	(1)

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Polycarbonate

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Optical properties	%		Initial / After 3 yr	(1)
		Light transmittance	85 / 82	
		Haze	3 / 19	
Dielectric constant	–	At 60 Hz	3.17	(1)
		At 1,000 Hz	2.9	
Volume resistivity	ohm cm	–	8×10^{16}	(1)
Surface tension γ	mN m^{-1}	20°C	42.9	(6)
		150°C	35.1	
		200°C	32.1	
Permeability coefficients	m^3 (STP) m s^{-1} m^{-2} Pa^{-1} ($\times 10^{17}$)	Gas (at 25°C)		(10)
		He	7.5	
		H_2	9.0	
		Ar	0.6	
		O_2	1.05	
		CO_2	6.0	
		N_2	0.225	
Diffusion coefficients	m^2 s^{-1} ($\times 10^{10}$)	Gas (at 25°C)		(10)
		H_2	0.64	
		Ar	0.015	
		O_2	0.021	
		CO_2	0.0048	
Solubility coefficients	m^3 (STP) m^{-3} Pa^{-1} ($\times 10^6$)	Gas (at 25°C)		(10)
		H_2	1.38	
		Ar	4.15	
		O_2	5.03	
		CO_2	124	
Thermal conductivity	W m^{-1} K^{-1}	–	0.192	(1)
Melt viscosity	Pa s	At 270°C	1,100	(1)
Speed of sound	m s^{-1}	Measured at room temperature and 1 MHz frequency		(3)
		Longitudinal	2,220	
		Shear	909	
Ignition temperature	K	–	651	(3)
Flammability	m s^{-1}	–	0.03	(1)
Oxygen index	%	–	25	(1)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Surface reradiation loss	$W\ m^{-2}$	–	11,000	(3)
Heat of gasification	$MJ\ mol^{-1}$	Flammability apparatus	0.53	(3)
Maximum use temperature	K	–	373–408	(1, 3)

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Polychloral

JAGATH K. PREMACHANDRA, CHANDIMA KUMUDINIE, AND JUNZO MASAMOTO

CLASS Polyacetals; poly(aldehydes)

STRUCTURE

$$\left(\begin{array}{c} CCl_3 \\ | \\ CH-O \end{array}\right)_n$$

MAJOR APPLICATIONS Potential material for engineering plastics with rodlike backbone. Possible use as a packing material for high-performance liquid chromatography.[1]

PROPERTIES OF SPECIAL INTEREST Crystalline material with mechanical properties comparable to engineering plastics with rigid backbone of 4_1 helix similar to that of isotactic polyacetaldehyde, completely isotactic nature, and clean degradation to monomer at elevated temperature. Optical activity of polychloral based on macromolecular asymmetry is a new development; the values of optical activity of these polymers is in the thousands of degrees.

OTHER POLYMERS SHOWING THIS SPECIAL PROPERTY Poly(*n*-hexyl isocyanate): rigid polymer backbone with bulky side chain. Triarylmethyl methacrylates: high value of optical activity with helix polymer structure.

Preparative Techniques*

Polymerization Process	Conditions	Reference
Anionic	Anionic polymerization is widely used. Initiators: alkali metal oxides, tertiary amines, tertiary phosphines, organometallic compounds, etc. Chloral is mixed with an anionic initiator above the threshold temperature, for bulk polymerization, and the mixture is then cooled (usually to 0°C under quiescent conditions). Thus, polychloral pieces of desired shape can be prepared.	(2-4)
Anionic	With lithium alkoxide of cholesterol at 0°C in hexane (0.2 mol% initiator relative to chloral)	(1)
Anionic	Oligomerization of chloral with lithium *t*-butoxide	(5, 6)
Anionic	Cooligomerization of chloral and bromal with lithium *t*-butoxide or bornyl oxide followed by acetate end-capping	(7)
Anionic	At −78°C using a series of organometallic catalysts, (3–45%) yield	(8)
Anionic	Initiator: lithium alkoxide of (-)borneol	(9)
	Initiators: H_2SO_4 and pyridine	(10)
Cationic	Initiators: BF_3, CH_3SO_3H, H_2SO_4 etc.	(2-4)

*For synthesis of the monomer, chloral (trichloro acetaldehyde), see reference (2).

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Ceiling temperature	K	In toluene	282	(2, 11)
		In tetrahydrofuran	284	
Enthalpy of polymerization	$kJ\,mol^{-1}$	From solution in toluene to partially crystalline polymer	37.8	(2, 11)
		From solution in tetrahydrofuran to polymer	14.6	
Entropy of polymerization	$J\,mol^{-1}\,K^{-1}$	From solution in toluene to partially crystalline polymer	134	(2, 11)
		From solution in tetrahydrofuran to polymer	52	
Typical comonomers	Most thoroughly studied family of polychloral copolymers are: chloral with isocyanates			(4, 12, 13, 14)
	Monochloroacetaldehyde and dichloroacetaldehyde			(15)
	Ketenes, formaldehyde, trioxane, etc.			(2)
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	147.5	–
Tacticity	–	X-ray diffraction, magic angle ^{13}C NMR and ^{35}Cl-NQR	Completely isotactic structure because of bulkiness of the trichloromethyl group	(2, 16)
		X-ray single crystal analysis, linear oligomers of chloral	Isotactic	(17)
Degree of polymerization	–	Catalyst $AlBr_3$, solvent CH_2Cl_2, at $-30°C$ for 5 h	190	(10)
		Catalyst $(C_4H_9)_3CH_3NI$, no solvent, at 0°C for 0.5 h	380	
		Catalyst 2,6-dimethoxyphenyllithium, solvent propylene, at $-48°C$ for 1 h	600	
IR (characteristic absorption frequencies)	cm^{-1}	CH bending	1,360	(18)
		C–O stretching	1,125	
		C–Cl stretching	682	
NMR	^{13}C NMR spectroscopy, solid-state at 100.5 MHz			(19)
	Cross polarization/magic angle spinning (CP/MAS) measurement			(19)
	^{13}C NMR, Fourier transform NMR spectrometer at room temperature and at 25 MHz. Internal standard: tetramethylsilane			(1)
	^{1}H and ^{13}C and 2D-NMR, at 35°C in $CDCl_3$ under a nitrogen atmosphere. Internal standard: tetramethylsilane			(5)
	^{1}H NMR, mixture of acetylated chloral addition products			(20)
	^{1}H and ^{13}C NMR, chloral oligomers prepared by lithium *t*-butoxide initiation			(21)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Mass spectrometry	Cooligomers of chloral and bromal (up to pentamers)			(7)
	Chloral oligomers by GC			(5)
	K+ ionization of desorbed species (K+IDS) spectrometry, linear *t*-butoxide-initiated, acetate-capped chloral oligomers, ion source pressure $< 10^{-6}$ Torr, source temperature = 200°C			(6)
	Amine-initiated chloral oligomers, K+IDS mass spectrometry and capillary GC			(22)
Thermal expansion coefficients	K^{-1}	–	4×10^{-5}	(2, 13)
Solvents	Completely insoluble in any organic solvent			(2)
	Copolymers of chloral with monochloroacetaldehyde is dissolved in $CHCl_3$			
Nonsolvents	Any organic solvent			(2, 23)
	Conventional organic solvents			(24)
	Any solvent			(1, 10)
	Chloral monomer			(2)
Lattice	–	–	Tetragonal	(25)
Space group	–	–	$I\,4_1/a$	(25)
Chain conformation	–	Helical, by IR spectroscopy		(10)
		4_1 helix similar to polyacetaldehyde, electron microscopy shows no evidence of chain folding or lamellar structure and small angle scattering suggests rodlike polymer		(2, 24, 25)
		4_1 helix, axis of helix is parallel to the *c*-axis of the crystal, by X-ray single crystal analysis, linear oligomers of chloral		(17)
		4_1 helix by X-ray studies on cold-rolled film samples		(25)
		4_1 helix by X-ray studies on film samples that were drawn over a hot pin at 180–210°C		(13)
		Helix symmetry 4_1, helix pitch (*c*-axis) 5.2 Å, monomer repeat (*c*-axis) 1.3 Å, and backbone atoms in monomer unit 2		(23)
Unit cell dimensions	Å	–	$a = 17.38$, $b = 6.45$	(25)
			$c = 5.2$	(2, 13, 23)
			$c = 4.81$	(17)
Unit cell contents (number of repeat units)			16	(25)
Degree of crystallinity	%	Wide angle X-ray diffraction of an oriented fiber	20–30	(2, 13)
		Depends upon the method of preparation	–	(10)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density (crystalline)	$g\,cm^{-3}$	Theoritical density	2.012	(13, 25)
		Observed density	1.9	(2, 13)
Glass transition temperature T_g	K	No T_g was observed between 123 and 473, and over 493		(13)
Melting point	K	Hypothetical melting point	733	(2, 13)
			>533	(23)
Vicat softening temperature	K	Onset of decomposition	473	(2, 13)
Tensile modulus	MPa	–	2,500–3,500	(2, 13)
		Chloral/dichloroacetaldehyde (DCA) copolymer, 28 mol% DCA	~1,100	(10)
		Chloral/DCA copolymer, 45 mol% DCA	~1,450	(10)
		Chloral/aromatic isocyanate (10%) copolymer	1,700–2,800	(13)
Shear modulus	MPa	Room temperature	850	(2, 13)
		−18°C	2,000	(2)
Tensile strength	MPa	–	35–50	(2, 13)
		Polychloral fibers	40	(2)
		Chloral/DCA copolymer, 28 mol% DCA	41.4	(10)
		Chloral/DCA copolymer, 45 mol% DCA	42	(10)
		Chloral/aromatic isocyanate (10%) copolymer	42–63	(13)
Yield stress	MPa	–	38	(2, 13)
Yield strain $(L/L_0)_y$	%	–	5	(13)
Maximum extensibility $(L/L_0)_r$	%	–	12–20	(2, 13)
		Chloral/DCA copolymer, 28 mol% DCA	12	(10)
		Chloral/DCA copolymer, 45 mol% DCA	12	(10)
		Chloral/aromatic isocyanate (10%) copolymer	15–45	(13)
Flexural modulus	MPa	–	2,200	(13)
Compressive strength	MPa	–	10	(13)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Notched Izod impact strength	$J\,m^{-1}$	—	60–80	(2, 13)
Hardness	—	Rockwell hardness	R10, M50	(13)
Index of refraction n	—	25°C	1.58	(2, 13)
Dielectric constant ε'	—	Room temperature	2.8	(2, 13)
Dissipation factor	—	—	0.003	(2, 13)
Optical activity: specific rotation $[\alpha]_d$	Degree	Using chiral lithium alkoxides as initiators	Thousands	(2)
			4,000 to −4,000	(26)
		Initiated with tetramethylammonium (-) acetyl mandelate, holding time = 10–50 min	+84 to +310 (a linear increase in specific rotation with time was observed)	(27)
		Initiated with tetramethylammonium (-) α-methoxy mandelate	Initial increase followed by a leveling off	(27)
		Holding time = 10–30 min	+136 to +163	(27)
		Holding time = 50 min	+114	(27)
		Initiated with lithium *R*(-)-2-octanoxide, holding temperature = 65°C, holding time = 10–70 min	~(4,300–1,000), higher holding times results in lower rotation values	(28)
		Initiated with lithium *R*(-)-2-octanoxide, holding temperature = 85°C, holding time = 10–70 min	~(2,300–500), higher holding temperatures results in lower rotation values	(28)
		Initiated with lithium *S*(+)-2-octanoxide, holding temperature = 85°C, holding time = 10–70 min	~(−2,000 to −800)	(28)
		Initiated with lithium (±)-2-octanoxide, holding temperature = 85°C, holding time = 10–70 min	Optically inactive	(28)
		Initiated with lithium cholestenoxide, holding time = 10–70 min		
		At 65°C	~(3,400–1,000)	(28)
		At 75°C	~(2,500–600)	(28)
		At 85°C	~(2,500–250)	(28)
		Using chiral initiators, solid films	Up to 5,000	(23)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Resistivity	ohm cm	—	4×10^{15}	(2, 13)
Coefficient of sliding friction μ	—	Both static and dynamic	0.55	(2, 13)
Pyrolyzability, nature of product	—	—	Clean degradation to chloral	(2, 18)
Pyrolyzability, amount of product	—	—	Clean degradation to chloral	(2, 18)
Decomposition temperature	K	Usually start to degrade by depoymerization to monomer	493	(2, 29, 30)
		20°C min^{-1}, properly end-capped and stabilized polymer under nitrogen atmosphere	523	(2, 29)
		20°C min^{-1}, maximum rate of degradation of properly end-capped and stabilized polymer under N_2 atmosphere	613	(2, 29)
Relative thermal decomposition rate	% min^{-1}	Acetate end-capped polymer	0.04	(10)
		Unend-capped polymer	1.48	
Flammability	—	—	Nonflammable	(13, 24)

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Polychloroprene

VASSILIOS GALIATSATOS

ALTERNATIVE NAMES, ACRONYMS, TRADE NAMES Poly(1-chloro-1-butenylene), poly(2-chloro-1,3-butadiene), chloroprene rubber (CR), GR-M, Baypren, Butaclor®, Neoprene, Perbunan C, Skyprene

CLASS Diene elastomers

STRUCTURE $-CH_2-Cl-C{=}CH-CH_2-$

MAJOR APPLICATIONS Aerospace industry (gaskets, seals, deicers); automotive industry (timing belts, window gaskets, fuel-hose covers, cable jacketing, sparkplug boots, hoses, and joint seals); industrial applications (pipeline pigs, gaskets, hoses, power transmission belts, conveyor belts, escalator handrails); and electronics (wire and cable jacketing). Also for sponge shoe soles and foam cushions.

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Type of polymerization	—	—	Emulsion polymerization		—
Typical initiator	—	—	$K_2S_2O_8$		—
Typical regulator	—	—	*n*-Dodecyl mercaptan		—
Typical comonomer	—	—	Sulfur		—
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	88.54		—
Typical molecular weight range of polymer	$g\,mol^{-1}$	—	1×10^5 to $>1 \times 10^6$		—
Tacticity	Major isomeric form is the trans-1,4 unit, which varies between 70 and 90% depending on temperature of polymerization. Remaining units are *cis*-1,4and -1,2 types.				—
Head-to-head content	%	—	10–15		—
Mark-Houwink parameters	$K = dL\,g^{-1}$		$K \times 10^5$	a	(1–4)
	a = None	Polychloroprene, toluene at 25°C	50	0.615	
		Linear polychloroprene, THF at 30°C	4.18	0.83	
		Neoprene CG, benzene	2.02	0.89	
		Neoprene GN, benzene	14.6	0.73	
		Neoprene W, benzene	15.5	0.71	

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Polychloroprene

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature	K	–	228–234	(5)
		Cooling rate = 0.3°C min^{-1} for the all *trans* polymer	228.5	
		1,4-*cis* polymer	253	
Melting temperature	K	Polymerization temperature range = −40 to 40°C	318–348	(6)
		1,4-*cis* polymer	343	
		All *trans* form	388, 380, and 353	
		Polymer prepared at −150°C	651	
Heat of fusion	kJ mol^{-1}	–	8.37	–
Unit cell dimensions	nm	Orthorhombic	$a = 0.884$, $b = 1.024$, $c = 0.48$	(7)
Unit cell content (number of repeat units)	–	–	4	–

^{13}C-NMR analysis of polychloroprenes* (8, 9)

Polymerization temp. (°C)	Total (%) (1,4-trans)	Inverted (%) (1,4-trans)	1,2	1,2 isomerized	3,4	*Cis*-1,4
90	85.4	10.3	2.3	0.6	4.1	7.8
40	90.8	9.2	1.7	0.8	1.4	5.2
20	92.7	8.0	1.5	0.9	1.4	3.3
0	95.9	5.5	1.2	1.0	1.1	1.8
(20	97.1	4.3	0.9	0.6	0.5	0.8
(40	97.4	4.2	0.8	0.6	0.5	0.7
10	–	–	–	–	–	–

*Resulting structure depends on polymerization temperature.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Mooney viscosity	°ML	–	47	–
Specific gravity	–	Neoprene WM1 (DuPont)	1.23	–
Thermal conductivity	W m^{-1} K^{-1}	20°C	0.19	–
Specific heat capacity	J K^{-1} kg^{-1}	–	2,175	–
Relative gas permeability and selectivity	–	Polychloroprene film at 23–25°C		–
		Helium vs. methane	5.0	
		Oxygen vs. nitrogen	3.64	
		Hydrogen vs. methane	7.69	
		Carbon dioxide vs. methane	8.5	

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Dose required to reduce the elongation at break to 50% of original	Gy	Low dose-rate conditions in air		3×10^5	(10)
		High dose rate or inert atmospheric conditions		5×10^5	
Flow behavior index n'	–	80°C		0.15	(11)
		100°C		0.11	
		120°C		0.07	
Consistency of flow K'	–	80°C		225.1	(11)
		100°C		257.6	
		120°C		279.6	
Shear viscosity	kPa s	Temp. (°C)	Shear rate (s^{-1})		(11)
		80	122.6	1.6	
		80	245.2	0.9	
		80	490.4	0.48	
		80	735.6	0.035	
		100	122.6	1.10	
		100	245.2	0.06	
		100	490.4	0.032	
		100	735.6	0.02	
		120	122.6	0.075	
		120	245.2	0.042	
		120	490.4	0.022	
		120	735.6	0.015	
Dynamic extensional viscosity	MPa s	Temp. (°C)	Shear rate (Hz)		(11)
		80.5	110	0.004	
		80.5	35	0.003	
		80	11	0.027	
		80	3.5	0.046	
		100	110	0.005	
		100	35	0.0025	
		100	11	0.038	
		100	3.5	0.042	
		120	110	0.002	
		120	35	0.004	
		120	11	0.03	
		120	3.5	0.025	
Scorch time	min	Mooney viscosity measured at 140°C, Δ5°ML		30	(12)
Minimum plasticity	°ML	–		43	(12)
Shrinkage on calendering	%	50°C		331	(12)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength	kg cm^{-2}	Vulcanization time		(12)
		5 min	179	
		10 min	210	
		15 min	190	
Elongation at break	%	Vulcanization time		(12)
		5 min	1,020	
		10 min	930	
		15 min	830	
300% modulus	kg cm^{-2}	Vulcanization time		(12)
		5 min	10	
		10 min	14	
		15 min	16	
500% modulus	kg cm^{-2}	Vulcanization time		(12)
		5 min	21	
		10 min	26	
		15 min	32	
Permanent set	%	Vulcanization time		(12)
		5 min	13	
		10 min	8	
		15 min	6	
Dielectric loss peaks	K	300 Hz		(12)
		α-relaxation	200 (in the glassy state)	
		β-relaxation	251 (above T_g)	
Extension dependence	K	Of the glass transition temperature in the dilatometric time scale	1.05–1.25	–
Anisotropy of segments and monomer units	$(\alpha_1 - \alpha_2)$ cm^3	α-Bromonapthalene	+110	(13)
		Carbon tetrachloride	+33	
		Chlorobenzene	+64	
		Dichloroethane	+39	
		α-Methylnapthalene	+99	
		Tetrachloroethylene	+46	
		Toluene	+67	
		p-Xylene	+88	

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Suppliers

Trade name	Supplier
Baypren	Bayer AG, Leverkusen, Germany Miles, Inc., Polymer Division, Pittsburg, Pennsylvania, USA
Butacor	A. Schulman, Akron, Ohio, USA
Neoprene	DuPont, Wilmington, Deleware, USA DuPont UK, Herts, United Kingdom
Perbunan C	Bayer AG, Leverkusen, Germany Miles, Inc., Polymer Division, Pittsburg, Pennsylvania, USA
Skyprene	Tosoh Corporation, Tokyo, Japan Tosoh USA, Inc., Atlanta, Georgia, USA

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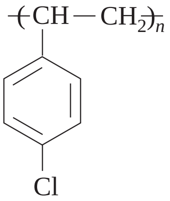
Poly(*p*-chlorostyrene)

JONATHAN H. LAURER AND RICHARD J. SPONTAK

ACRONYMS *p*-CST, PCS, *p*-ClST, *p*-ClSt

CLASS Vinyl polymers; *p*-halostyrenes

STRUCTURE



MAJOR APPLICATIONS High-contrast negative e-beam resist.[1] Comonomer in numerous block copolymer systems.[2,3]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	$\overline{M}_w = 650{,}000\,g\,mol^{-1}$	1.246	(4)
Specific free volume	$cm^3\,g^{-1}$	$\overline{M}_w = 650{,}000\,g\,mol^{-1}$	0.124	(4)
^{13}C NMR chemical shift δ	ppm	For β-carbon, δ	114.4	(5)
Thermal expansion parameter α	K^{-1}	–	0.582	(6)
Ionization potential I_p	eV	–	8.45	(7)
Heat capacity increase ΔC_p	$J\,K^{-1}\,mol^{-1}$	At T_g 300 K to T_g T_g to 550 K	31.1 $-4.20 + 0.4866T$ $112.57 + 0.2775T$	(8)
γ-Loss peak	K	–	143	(9)

Dynamic elastic shear modulus* compared to linear polystyrene[9]

T (°C)	Poly(*p*-chlorostyrene) G' (MPa)	Linear polystyrene G' (MPa)
−78	1,400	1,260
−98	1,420	1,280
−123	1,420	1,320
−148	1,450	1,350
−173	1,500	1,350

*Calculated from the frequencies of free vibration, moment of inertia of the system, and room-temperature polymer dimensions. Measurements performed on a torsion pendulum at a constant frequency of 1 Hz.

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Solubility parameters δ	$(MPa)^{1/2}$	$T = 25°C$		19.7	(10)
		$T = 25°C$; (group contribution calculation)		20.0	(6)
		$T = 160°C$; (experimental)		12.3	(6)
Theta temperature θ	K	Composition (v/v) by phase equilibria method			
		Benzene		281	(11)
		Benzene/Methanol (4.5/1)		314.6	(11)
		Benzene/Methanol (5.0/1)		305.4	(11)
		Benzene/Methanol (5.5/1)		299.7	(11)
		Carbon tetrachloride		323.7	(12)
		Cumene		332	(13)
		Ethyl carbitol		300.8	(12)
		Ethyl chloroacetate		271.2	(12)
		Ethylbenzene		258.3	(12)
		Isopropyl acetate		348.5	(12)
		Isopropyl benzene		332	(12)
		Isopropyl chloroacetate		264.8	(12)
		Methyl chloroacetate		337.6	(12)
		n-Butyl carbitol		323.1	(12)
		t-Butyl acetate		338.4	(12)
		Tetrachloroethylene		317.4	(12)
Second virial coefficient A_2	$mol\,cm^3\,g^{-2}$	Solvent			(10)
		Toluene		1.20	
		Methylethylketone		1.72	
		Cumene		−0.20	
Flory–Huggins interaction parameter χ	–	Solvent	T (°C)		
		t-Butyl acetate	30	0.462	(12)
		n-Butylcarbitol	30	0.468	(12)
		Ethylcarbitol	30	0.505	(12)
		Ethyl chloroacetate	30	0.464	(12)
		Isopropyl acetate	30	0.446	(12)
		Isopropyl chloroacetate	30	0.460	(12)
		Toluene	30	0.460	(10)
			150	0.294	(6)
			160	0.270	(6)
			170	0.233	(6)
		Methylethylketone	30	0.447	(10)
		Methyl chloroacetate	30	0.549	(12)
		Cumene	55	0.505	(10)
		Carbon tetrachloride	30	0.528	(12)
		n-Pentane	150	0.600	(6)
			160	0.540	(6)
			170	0.470	(6)
		n-Hexane	150	0.755	(6)
			160	0.694	(6)
			170	0.641	(6)

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Flory–Huggins interaction parameter χ	—	Solvent	T (°C)		
		n-Heptane	150	0.843	(6)
			160	0.798	(6)
			170	0.771	(6)
		Benzene	150	0.305	(6)
			160	0.271	(6)
			170	0.225	(6)
		Ethylbenzene	30	0.474	(12)
		Isopropylbenzene	30	0.478	(12)
			150	0.491	(6)
			160	0.473	(6)
			170	0.455	(6)
		n-Propylbenzene	150	0.497	(6)
			160	0.472	(6)
			170	0.429	(6)
		Tetrachloroethylene	30	0.618	(12)
	—	Monomer or polymer	T (°C)		
		Phenylene oxide	200	0.030	(2)
		Phenylsulfonylated phenylene oxide	200	0.017	(2)
		o-Chlorostyrene	150	0.0915	(3)
			200	0.0940	(2, 3)
			250	0.109	(3)
			300	0.135	(3)
		Styrene	150	0.0720	(3)
			200	0.0792	(3)
			250	0.0927	(3)
			300	0.111	(3)
Interaction parameter χ_{12}^{*} based on hard-core volumes	—	Solute	T (°C)		(6)
		n-Pentane	150	0.965	
			160	0.951	
			170	0.941	
		n-Hexane	150	1.047	
			160	1.016	
			170	0.996	
		n-Heptane	150	1.085	
			160	1.064	
			170	1.061	
		Toluene	150	0.478	
			160	0.466	
			170	0.451	
		Benzene	150	0.517	
			160	0.503	
			170	0.479	
		Isopropylbenzene	150	0.640	
			160	0.635	
			170	0.632	

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Interaction parameter χ_{12}^* based on hard-core volumes	–	Solute	T (°C)		(6)
		n-Propylbenzene	150	0.641	
			160	0.629	
			170	0.608	
Glass transition temperature T_g	K	$\overline{M}_w \times 10^{-4}$ (g mol^{-1})	$\overline{M}_n \times 10^{-4}$ (g mol^{-1})		
		8.7	16.0	405	(2)
		16.4	8.0	402	(7)
		25.26	6.16	388	(14)
		26.7	14.0	406	(8)
		65.0	–	399	(4)

Intrinsic viscosity [η]; and partial specific volume ν_p

Solvent	$\overline{M} \times 10^{-4}$ (g mol^{-1})	T (°C)	ν_p (cm^3 g^{-1})	[η] (dl g^{-1})	Reference
Toluene	33.0*	30	0.778	0.557	(10)
Methylethylketone	33.0*	30	0.770	0.603	(10)
Cumene	33.0*	55	0.788	0.354	(10)
Chloroform	14.04*	25	–	0.79	(8)
Benzene	179.9†	27	–	0.963	(11)
	129.7†	27	–	0.793	(11)
	81.7†	27	–	0.617	(11)
	48.9†	27	–	0.466	(11)
	34.1†	27	–	0.375	(11)
	179.9†	32	–	1.020	(11)
	129.7†	32	–	0.825	(11)
	81.7†	32	–	0.626	(11)
	48.9†	32	–	0.481	(11)
	34.1†	32	–	0.383	(11)
	179.9†	42	–	1.059	(11)
	129.7†	42	–	0.863	(11)
	81.7†	42	–	0.649	(11)
	48.9†	42	–	0.484	(11)
	34.1†	42	–	0.390	(11)
Experimental fits	–				
Toluene	–	30	–	$(12.3 \times 10^{-5})\overline{M}_w^{0.65}$	(13)
Ethylbenzene		30		$(21.7 \times 10^{-5})\overline{M}_w^{0.60}$	(13)

*Number-average molecular weight.
†Viscosity-average molecular weight.

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Permeability coefficient P	cm^3(STP) cm $(cm^2\ s\ cm\ Hg)^{-1}$	$\overline{M}_w = 650,000\ g\ mol^{-1}$, measured at 1 atm, 35°C				(4)
		Gas				
		He			16.4×10^{-10}	
		CH_4			2.6×10^{-11}	
		O_2			1.2×10^{-10}	
		N_2			2.3×10^{-11}	
		CO_2			4.3×10^{-10}	
Diffusion coefficient D	$cm^2\ s^{-1}$	$\overline{M}_w = 650,000\ g\ mol^{-1}$, measured at 1 atm, 35°C				(4)
		Gas				
		CH_4			6.1×10^{-9}	
		O_2			7.8×10^{-8}	
		N_2			2.4×10^{-8}	
		CO_2			2.2×10^{-8}	
Refractive index (n) increment, and dielectric constant (ε) increment, (C = *p*-ClSt weight fraction in solvent)	–	Solvent	T (°C)	dn^2/dc	$d\varepsilon/dc$	(15)
		Benzene	15	0.271	2.237	
			25	2.277	1.869	
			35	0.283	1.757	
			50	0.290	1.712	
			60	0.291	1.722	
			70	0.296	1.668	
		Isopropyl benzene	30	0.295	1.735	
			50	0.296	1.685	
			60	0.297	1.665	
			70	0.300	1.588	
			80	0.301	1.534	
			90	0.301	1.438	
		n-Propyl benzene	20	0.291	1.644	
			30	0.292	1.600	
			40	0.296	1.597	
			50	0.297	1.569	
			60	0.298	1.552	
			70	0.298	1.513	
			80	0.299	1.453	
			90	0.302	1.392	
Mean square dipole moment ratio, $D_\infty = \langle\mu^2\rangle/x\mu_0^2$	–	Solvent	T (°C)			(15)
		Benzene	15	0.599		
			25	0.513		
			35	0.501		
			50	0.521		
			60	0.556		
			70	0.562		

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Mean square dipole moment ratio, $D_\infty = \langle\mu^2\rangle/x\mu_0^2$	—	Solvent	T (°C)		(15)
		Isopropyl benzene	30	0.493	
			40	0.513	
			50	0.521	
			60	0.540	
			70	0.534	
			80	0.537	
			90	0.520	
		n-Propyl benzene	20	0.436	
			30	0.445	
			40	0.465	
			50	0.478	
			60	0.496	
			70	0.505	
			80	0.503	
			90	0.499	

Preparative techniques

Living cationic polymerization

Initiating system	1-Phenylethyl chloride/$SnCl_4$
Solvent	Methylene chloride
Temperature	0°C
Reagent concentrations	[*p*-ClSt] = 1.0 M, [1-phenylethyl chloride] = 20 mM, [$SnCl_4$] = 100 mM
% Conversion	80% in 2 h
Molecular weight range	10^3–10^4 g mol^{-1}
$\overline{M}_w/\overline{M}_n$	1.1
Reference/Note	(5)/Authors also report living polymerization at 25°C

Living carbocationic polymerization

Initiating system	Cumyl methyl ether/BCl_3
Solvent	Methylene chloride
Temperature	−60°C
Reagent concentrations	[Cumyl methyl ether] = 4.92×10^{-3} M, [BCl_3] = 0.104 M
% Conversion	66–72
Molecular weight range	4,190–12,390 g mol^{-1}
$\overline{M}_w/\overline{M}_n$	1.40–1.79
Reference/Note	(16)/Authors attribute high $\overline{M}_w/\overline{M}_n$ to slow cationation

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Living carbocationic polymerization

Initiating system	**2-Chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ + dimethylacetamide (DMA) (electron donor) + 2,6-*di*-*t*-butylpyridine (DtBP) (proton trap)**
Solvent	Methyl chloride/methylchlorohexane
Temperature	$-80^{\circ}C$
Reagent concentrations	[TMPCl] = 5.4 mM, [$TiCl_4$] = 0.086 M, [DMA] = 4.3 mM, [DtBP] = 3.6 mM
% Conversion	97–100%
Molecular weight range	3,500–7,670 $g\,mol^{-1}$
$\overline{M}_w/\overline{M}_n$	1.26–1.51
Reference/Notes	[16]/$TiCl_4$ is moisture sensitive compared to BCl_3

Photochemical polymerization

Initiating system	**Polymethylphenylsilane (PMPS): UV λ = 300–400 nm**
Solvent	In bulk
Temperature	$30^{\circ}C$
Reagent concentrations	[*p*-ClSt] = 7.96 M, [PMPS] = 0.39–1.50 M
Molecular weight range	50,000–85,500 $g\,mol^{-1}$
$\overline{M}_w/\overline{M}_n$	2.09–2.63
Reference	(17)

Typical comonomers used in copolymerizations

Comonomer	**Reference**
Citraconic anhydride	(18)
Styrene	(7, 19, 20)
Maleic anhydride	(21)
o-Chlorostyrene	(3)

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Poly(chlorotrifluoroethylene)

ANTHONY L. ANDRADY

ACRONYM, TRADE NAME PCTFE, Kel-F 81 (3M Company)

CLASS Vinylidene polymers

STRUCTURE $(-CF_2CFCl-)$

MAJOR APPLICATIONS Used to mold equipment parts, seals, and gaskets, particularly in chemical process equipment and in cryogenic systems. Also used as barrier packaging in pharmaceutical industry. Elastomeric homo- and copolymers used in o-rings, gaskets, and diaphragms.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Radical polymerization	–	Bulk polymerization with the initiators		
		Trichloroacetyl peroxide		(1)
		Dichlorotrifluoropropionyl peroxide		(2)
Typical comonomers	Vinylidene fluoride (Kel-F 800, 3M Company) Ethylene (Halar, Aclar, Allied Corporation)			–
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	116.47	–
Typical molecular weight range of polymer	$g\,mol^{-1}$	–	$7–40 \times 10^4$	(3)
Solvents	Cyclohexane (235°C), benzene (200°C), toluene (142°C), 1,1,1-trichloroethane (120°C), carbon tetrachloride (114°C)			(4–7)
Nonsolvents	Hydrocarbons, alcohols		–	
Crystalline structure	nm	Pseudohexagonal structure	$a = 0.644$, $c = 4.15$	(8)
Degree of crystallinity	%	Commercial polymer	40–80	(3)
Heat of fusion	$kJ\,mol^{-1}$	–	5.021	(9)
Entropy of fusion	$kJ\,mol^{-1}$	–	0.0104	(9)
Density (crystalline)	$g\,cm^3$	Estimate for completely crystalline polymer	2.187	(10)
		Estimate for completely amorphous polymer	2.077	
Avrami exponent	–	Dilatometry 180–196°C	3	(11)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature	K	Sample with ~80% crystallinity (dynamic mechanical at 1 Hz)	423	(12)
Melting transition temperature	K	Differential thermal analysis	483–488	(13)
Sub-T_g transitions	K	Sample with ~80% crystallinity		
		Dynamic mechanical (1 Hz)		(12)
		β transition	363	
		γ transition	236	
		Mechanical loss		(14)
		β transition	368	
		γ transition	230	
Heat capacity	$kJ\,K^{-1}\,mol^{-1}$	100°C	0.0363	(15)
		200°C	0.0575	
		250°C	0.0690	
Tensile modulus	MPa	−196°C	7,660	(8)
		25°C	14,000	(13)
Tensile strength	MPa	−196°C	119–173	(8)
		25°C	40	(13)
		125°C	4	–
Elongation	%	−196°C	2–4	(8)
		25°C	150	(13)
		125°C	400	–
Flexural modulus	MPa	ASTM D790		(13)
		23°C	1,250	
		−196°C	14,420	
Flexural strength	MPa	–	74	(13)
		−190°C	400	(16)
Permeability coefficient P	m^3 (STP) $m\,s^{-1}\,m^{-2}\,Pa^{-1}$ ($\times10^{-17}$)	Unplasticized film, ~30% crystalline	0.705	(16)
		H_2, 20°C	0.0038	(17)
		N_2, 25°C		
		O_2, 40°C	0.03	(17)
		CO_2, 40°C	0.158	(17)
		H_2O, 25°C	0.218	(18)
		Unplasticized film, ~80% crystalline		
		N_2, 25°C	0.0023	(17)
		O_2, 40°C	0.0188	(17)
		CO_2, 40°C	0.036	(17)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Pyrolyzability	The main decomposition product is monomer (26% by weight). Halocarbon waxes also formed			(19)
Thermal decomposition temperature	K	–	623–643	(19)

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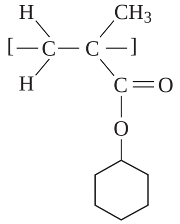
Poly(cyclohexyl methacrylate)

JIANYE WEN

ACRONYM PCHMA

CLASS Vinylidene polymers

STRUCTURE



MAJOR APPLICATIONS Adhesives and binders, coatings, optical waveguides, and blends with other polymers for various applications.

PROPERTIES OF SPECIAL INTEREST Hard; T_g similar to poly(methyl methacrylate) but much higher T_g than its *n*-hexyl isomer because of the bulkiness of the cyclohexyl group.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	168	—
Coefficient of thermal expansion	K^{-1} ($\times 10^{-4}$)	20°C	2.4	(1)
		40°C	2.5	
		60°C	2.5	
		80°C	2.5	
		120°C	5.6	
		140°C	6.0	
		160°C	6.2	
		180°C	6.3	
		200°C	6.4	
Compressibility	bar^{-1} ($\times 10^{-5}$)	20°C, glassy state	2.5	(1)
		40°C, glassy state	2.7	
		60°C, glassy state	2.8	
		140°C	6.3	
		160°C	7.0	
		180°C	7.7	
		200°C	8.6	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Decomposition temperature	K	Initial	463	(2)
		–	473	(3)
		50%	543	(2)
		Max	557, 629, 719	(3)
		–	623	(2)
Density	$g\,cm^{-3}$	20°C	1.100	(4, 5, 6)
		40°C	1.095	(1)
		80°C	1.084	(1)
		120°C	1.066	(1)
		140°C	1.054	(1)
		160°C	1.041	(1)
		180°C	1.028	(1)
		200°C	1.015	(1)
		110–199°C	$1.1394 - (5.90 \times 10^{-4})t - (0.163 \times 10^{[} - 6)t^2$	(1)
Glass transition temperature T_g	K	–	384	(3)
		Atactic	377	(5, 7, 8)
		Syndiotactic	436	(5, 7)
		Isotactic	324	(5, 7)

Mark-Houwink parameters: K and a

Solvent	Temp. (°C)	Mol. wt. range ($M \times 10^{-4}$)	$K \times 10^3$(ml g^{-1})	a	Reference
Benzene	30	–200	8.4	0.69	(9)
	25	–419	3.54	0.77	(10)
Butanol	23 (θ)	–445	33.7	0.50	(11)
	22.5 (θ)	–125	45.2	0.50	(12)
	25	–125	31.8	0.533	(12)
Butanone	25	–560	5.79	0.68	(11)
	30	–200	7.0	0.66	(9)
Cyclohexane	25	–418	8.8	0.67	(10)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molar refraction (R)	cm^3	–	45.05	(13)
Molar volume (V_m)	$cm^3\,mol^{-1}$	–	150.80	(13)
Index of refraction n_{25}^{D}	–	–	1.50645	(4, 6, 14)
			1.5066	(15)

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Theta solvent	—	*n*-Butanol		22.5°C	(12)
				23°C	(11)
		n-Decane		93.6°C	(16)
				120.0°C	(17)
		n-Decanol		23.0°C	(16)
		n-Dodecane		97.5°C	(16)
				129.9°C	(17)
		n-Hexanol		9.2°C	(16)
		n-Nonanol		20.2°C	(16)
		n-Octanol		17.9°C	(16)
		n-Octane		83.4°C	(16)
				112.1°C	(17)
		n-Propanol		39.5°C	(16)
Solvents	Tetrachloromethane, toluene, tetrahydrofuran, benzene, chloroform, methyl ethyl ketone, and cyclohexanone				(2)
Nonsolvents	Hexane, dimethylformamide, and methanol				(2)
Unperturbed dimension	$[\eta]/M^{1/2} \times 10^4$	Solvent	Temp. (°C)		(17)
		n-Propanol	39.2	4.88	
		n-Butanol	22.7	4.58	
		n-Hexanol	9.2	4.37	
		n-Ocanol	17.0	4.51	
		n-Nonanol	19.8	4.56	
		n-Decanol	23.0	4.66	
		n-Octane	112.1	4.08	
		n-Decane	120.0	4.18	
		n-Dedecane	129.9	4.36	

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Poly(di-*n*-butylsiloxane)

YULI K. GODOVSKY AND VLADIMIR S. PAPKOV

ACRONYM PDBuS

CLASS Polysiloxanes

STRUCTURE $[-(C_4H_9)_2SiO-]$

PROPERTIES OF SPECIAL INTEREST Low glass transition temperature, mesophase behavior.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Preparative technique	Anionic ring-opening polymerization of hexabutylcyclotrisiloxane			(1–4)
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	158.31	–
Typical molecular weight range of polymer	$g\,mol^{-1}$	–	10^4–10^5	–
NMR spectroscopy	Solid state ^1H, ^{13}C, ^{29}Si			(3, 4)
Heat of fusion	$kJ\,mol^{-1}$	High temperature crystal 2 to mesophase	0.9–1.1	(3–5)
Entropy of fusion	$J\,mol^{-1}\,K^{-1}$	–	3.9	(3–5)
Glass transition temperature	K	DSC	157	(3)
Melting temperature	K	High temperature crystal 2 to mesophase	254	(3–5)
Polymorphs		Low-temperature crystal 1; DSC, X-ray data		(3–6)
		High temperature crystal 2		(3–6)
		Mesophase		(3–6)
Transition temperature	K	Crystal 1–crystal 2, DSC	229	(3–5)
Heat of transition	$kJ\,mol^{-1}$	Crystal 1–crystal 2	3.6	(3–5)
Isotropization temperature	K	Polarization microscopy		(3)
		Strong MW dependence		
		2.8×10^4	489	
		1.28×10^5	572	

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Poly(diethylsiloxane)

YULI K. GODOVSKY AND VLADIMIR S. PAPKOV

ACRONYM PDES

CLASS Polysiloxanes

STRUCTURE $[-(C_2H_5)_2SiO-]$

MAJOR APPLICATIONS Comonomer for low-temperature silicone rubbers: for example, poly(dimethyl-diethyl)siloxane. Low molecular weight PDES is used in Russia as basis for low- and high-temperature silicone oils, greases, and lubricants.[1]

PROPERTIES OF SPECIAL INTEREST Low glass transition temperature, mesophase behavior including reversible stress-induced mesophase formation accompanied by necking-denecking phenomena in cyclic deformation of elastomers at room temperature and above.[2,3]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Preparative technique	Anionic ring-opening polymerization of hexaethylcyclotrisiloxane			(4–7)
Enthalpy of polymerization	$kJ\,mol^{-1}$	$T_{pol} = 443\,K$	15.1 ± 0.4	(8)
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	102.21	–
Typical molecular weight range of polymer	$g\,mol^{-1}$	–	2×10^3–1×10^6	–
Typical polydispersity index (M_w/M_n)	–	–	1.1–2.0	(4–7, 9)
Raman spectroscopy	Temperature range: 129–293 K			(10)
IR spectroscopy	Temperature range: 129–303 K			(11)
NMR spectroscopy	Solid state ^1H, ^{13}C, ^{29}Si			(6, 12–15)
Density (amorphous)	$g\,cm^{-3}$	293 K	0.99	(5, 16)
Thermal expansion coefficient	K^{-1}	293 − 363 K (dilatometry); pressure $P = 0$–$0.1\,GPa$ (mesophase state and isotropic melt)	$(6.3 - 17P) \times 10^{-4}$	(16)
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None	Toluene, 25°C, MW = $(1.15$–$3.7) \times 10^5$	$K = 2.71 \times 10^{-2}$ $a = 0.636$	(17)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Characteristic ratio $\langle r^2 \rangle / nl^2$	—	Toluene, 25°C	7.9	(17)
Temperature dependence of the unperturbed dimensions of chains, $d \ln \langle r^2 \rangle_0 / dT$	—	Stretching calorimetry, 25–100°C	-0.80×10^3	(18)
Energy contribution f_u/f	—	Stretching calorimetry, 25–100°C	−0.25	(18)

Unit cell dimensions[19]

Polymorphs	Lattice	Monomers per unit cell	Cell dimension (Å)			Cell angles (degrees)		
			a	***b***	***c*** **(chain axis)**	α	β	γ
α_1	Monoclinic	2	14.45	8.75	4.72	90	90	29.8
α_2	Monoclinic	2	14.59	8.90	4.75	90	90	29.7
β_1	Tetragonal	2	7.83	7.83	4.72	90	90	90
β_2	Tetragonal	2	7.90	7.90	4.72	90	90	90
μ (mesophase)	Monoclinic (close to pseudohexagonal)	2	14.75	8.89	4.88	90	90	31.2

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Degree of crystallinity	%	Cold crystallization after quenching amorphous sample	≈30	(5, 19, 20)
		Crystallization from mesomorphic state	>90	
Heat of fusion	$kJ\,mol^{-1}$	$\alpha_2 \rightarrow \mu$	1.72	(5, 6)
		$\beta_2 \rightarrow \mu$	2.14	
Heat of isotropization	$kJ\,mol^{-1}$	$\mu \rightarrow$ isotropic melt	0.31	(5, 6, 21)
Entropy of fusion	$J\,mol^{-1}\,K^{-1}$	$\alpha_2 \rightarrow \mu$	6.14	(5, 6, 21)
		$\beta_2 \rightarrow \mu$	7.38	(5, 6)
Entropy of isotropization	$J\,mol^{-1}\,K^{-1}$	$\mu \rightarrow$ isotropic melt	0.92	(5, 6, 21)
Density (crystalline)	$g\,cm^{-3}$	From X-ray data		(19)
		α_1, < 212 K	1.17	
		α_2, 223 K	1.10	
		β_1, 193 K	1.17	
		β_2, 223 K	1.14	
Density (mesophase)	$g\,cm^{-3}$	μ, 293 K	1.02	(19)

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Poly(diethylsiloxane)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature	K	DSC	134	(5)
		Adiabatic calorimetry	130	(8, 22)
		Dielectric, 1 KHz	146	(11)
		Dielectric, 100 Hz	133	(23)
		NMR, T_1 and T_2	138–140	(13, 22)
		DMA, 1 Hz	134	(11)
Melting temperature	K	$\alpha_2 \rightarrow \mu$, MW = 1.6 × 105	280	(5, 21)
		$\beta_2 \rightarrow \mu$	290	
Transition temperature	K	$\alpha_1 \rightarrow \alpha_2$	214	(5, 21)
		$\beta_1 \rightarrow \beta_2$	206	
Heat of transition	$kJ\,mol^{-1}$	$\alpha_1 \rightarrow \alpha_2$	2.86	(5, 21)
		$\beta_1 \rightarrow \beta_2$	2.65	
Isotropization temperature	K	MW ($\times 10^3$) =		(5, 21, 24)
		765	326	
		425	325	
		172	319	
		100	307	
		58	296	
		≈25	No mesophase	
Avrami exponent *n*	–	Crystallization at 276 K from mesophase	≈2	(21)
		Formation of mesophase from the melt at 293–306 K	1.75	
Heat capacity	$J\,K^{-1}\,mol^{-1}$ (of repeat units)	β_1 polymorph		(8, 22, 25)
		10 K	2.289	
		20 K	10.97	
		50 K	39.60	
		100 K	75.40	
		200 K	123.0	
		β_2 polymorph		(8, 22, 25)
		250 K	140.5	
		330 K (melt)	174.0	
		ΔC_p at T_g	36.0	(5, 8)
Dielectric constant ε'	–	83–123 K	2.60–2.70	(23)
Loss factor tan δ	–	200–300 K	0.015	(11)
Viscosity	Pa s	MW = 6.69×10^5, rate of shear $10^{-4}\ s^{-1}$		(26)
		Mesophase (20°C)	2×10^8	
		Melt (60–100°C)	5×10^5	

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Poly(di-*n*-hexylsiloxane)

YULI K. GODOVSKY AND VLADIMIR S. PAPKOV

ACRONYM PDHeS

CLASS Polysiloxanes

STRUCTURE $[-(C_6H_{13})_2SiO-]$

PROPERTIES OF SPECIAL INTEREST Low glass transition temperature, mesophase behavior.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Preparative technique	Anionic ring-opening polymerization of hexahexylcyclotrisiloxane			(1, 2)
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	214.41	–
Typical molecular weight range of polymer	$g\,mol^{-1}$	–	10^4–10^6	–
NMR spectroscopy	Solid state ^{29}Si			(2, 3)
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ $a =$ None	Toluene, 298 K	$K = 0.275$ $a = 0.463$	(3)
Heat of fusion	$kJ\,mol^{-1}$	High temperature crystal 2 to mesophase	1.8–2.2	(3–5)
Entropy of fusion	$J\,mol^{-1}\,K^{-1}$	–	7.2	(3–5)
Glass transition temperature	K	DSC	168	(5)
Melting temperature	K	High temperature crystal 2 to mesophase	296	(3–5)
Polymorphs	Low temperature crystal 1; DSC, X-ray data High temperature crystal 2 Mesophase			(3–5) (3–5) (3–5)
Transition temperature	K	Crystal 1–crystal 2, DSC	246	(3–5)
Heat of transition	$kJ\,mol^{-1}$	Crystal 1–crystal 2	6. 7	(3)
Isotropization temperature	K	Polarization microscopy	603	(3)

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Poly(di-*n*-hexylsilylene)

ROBERT WEST

ACRONYM, ALTERNATIVE NAME PDHS, polydi-*n*-hexylsilane

CLASS Polysilanes

STRUCTURE $[-nC_6H(13-Si-nC_6H_{13}-]$

MAJOR APPLICATIONS None

PROPERTIES OF SPECIAL INTEREST Transition from crystalline phase to columnar mesophase at 42°C. That is, PDHS is crystalline with an all-*trans* arrangement of the polysilane chain below the disordering temperature of 42°C; above this temperature the polymer exists in a hexagonal columnar liquid crystalline phase.

For general information about polysilane polymers see the entry for *Poly(methylphenylsilylene)* in this handbook.

Preparative techniques

REACTANTS	TEMP. (°C)	YIELD (%)	M_w	M_w/M_n	REFERENCE
n-Hex_2SiCl_2, Na, toluene, 15-crown-5	110	24	—	—	(1)
n-Hex_2SiCl_2, Na, toluene, 15-crown-5, ultrasound	20	50	67,000	—	—
n-Hex_2SiCl_2, Na, toluene (25% diglyme)	24	—	45,000	1.73	(2)
Same as above with 3% 18-crown-6	—	63.4	9,200	3.6	(2)
n-Hex_2SiCl_2, Na, Et_2O, 15-crown-5	35	22	23,800	—	(3)
n-Hex_2SiCl_2, Na, toluene, 2% EtOAc	110	12.6	1,300,000	1.8	(4)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Repeat unit	g mol^{-1}	$(C_6H_{13})_2Si$	198	—
Infrared spectrum	cm^{-1}	—	2,961, 2,924, 2,871, 2,854, 1,471, 1,417, 1,379, 1,233, 1,175, 1,110, 977, 899, 727, 673	(5)
UV absorption	λ_1 (nm)	Hexane, $\varepsilon = 9{,}700$	318	(2)
Emission spectrum	λ_1 (nm)	Hexane, $\phi = 0.42$, $\tau = 150$ ps	342	(6)

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
NMR spectra	δ (ppm)	Nucleus	Conditions	Temp. (°C)		
		^{29}Si	Solution, trichlorobenzene-dioxane-d_8	25	−24.8	(7)
		^{29}Si	Solid	25	−20.8	(8)
				44.3	−24.1	(8)
		^{13}C	Solution, trichlorobenzene-dioxane-d_8	25	14.45 23.49 32.55 35.19 28.41 15.92	(7)
		^{1}H	Solution, $CDCl_3$	25	0.6–1.7	(2)
Solvents	THF, toluene, CH_2Cl_2, hexane					
Nonsolvents	Ethanol, 2-propanol					
Properties from light scattering study						(9)
M_w	g mol^{-1}	Hexane			2.2×10^6	
M_w/M_n	–	–			2.3	
dn/dc	ml g^{-1}	–			0.138	
A_2	ml mol g^{-2}	–			1.62×10^{-4}	
R_g	nm	–			10^8	
$\lambda_{persist}$	nm	–			6–7	
M_w	g mol^{-1}	THF			2.2×10^6	
M_w/M_n	–	–			2.3	
dn/dc	ml g^{-1}	–			0.177	
A_2	ml mol g^{-2}	–			1.14×10^{-1}	
R_g	nm	–			92	
l/k	nm	–			5.4	
C_∞	nm	–			19	
Crystalline properties	Monoclinic lattice below transition temperature of 42°C Hexagonal columnar mesophase above transition temperature					
Crystalline phase	Å	25°C			$a = 13.75$, $b = 21.82$, $c = 4.07$	(10, 11)
	Degrees	25°C			$\gamma = 88$	(10, 11)
Hexagonal columnar mesophase, a	Å	>42°C			1.56	(10, 11)
Surface tension	mN m^{-1}	–			29.9	(12)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Scission, quantum yield, ϕ_s	mol Einstein^{-1}	Toluene solution, $\lambda = 353$ nm	0.6	(6)
Cross-linking, quantum yield, ϕ_x	mol Einstein^{-1}	Toluene solution, $\lambda = 353$ nm	0	(6)
Suppliers	Gelest, Inc., 612 William Leigh Drive, Tullytown, PA 19007-6308, USA			

Nonlinear optical properties[13]

M_w (g mol^{-1})	Temp. (°C)	λ (nm)	Lp (thickness, nm)	X^{131} (esu$^{(\times 10-12)}$)
>300,000	23	1,064	50	11
	21	1,064	120	5.5
	50	1,064	120	2.0
	23	1,064	240	4.6
		1,907	240	1.3
		1,907	240	0.9

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Poly(dimethylferrocenylethylene)

IAN MANNERS

CLASS Inorganic and semi-inorganic polymers

STRUCTURE $[(C_5H_3Me)Fe(C_5H_3MeCH_2CH_2)]_n$

PROPERTIES OF SPECIAL INTEREST Low cost; ease of synthesis; and interesting optical, magnetic, and electrical properties.

SYNTHESIS Poly(dimethylferrocenylethylene) can be synthesized via the thermal ring opening polymeriztion (ROP) of the strained ethylene bridged dimethyl[2]ferrocenophane, $(C_5H_3Me)_2FeCH_2CH_2$.[1]

PROPERTY	UNITS	CONDITION	VALUE	REFERENCE
UV-vis absorption, λ_{max}	nm	THF solution	440	(1)
UV-vis absorption coefficient, ε	$M^{-1}\,cm^{-1}$	THF solution	190	(1)
Glass transition temperature	K	DSC experiment	338	(1)
Unit cell dimensions		For monomer $(C_5H_4)_2FeCH_2CH_2$		
Lattice	—	—	Orthorhombic	—
Monomers per unit cell	—	—	8	—
Cell dimensions	Å	—	$a = 7.421$	—
			$b = 12.305$	—
			$c = 19.839$	—
Cell angles	Degrees	—	$\alpha = \beta = \gamma = 90$	—

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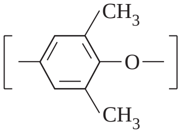
Poly(2,6-dimethyl-1,4-phenylene oxide)

ALLAN S. HAY AND YONG DING

ACRONYMS PPO, PPE

CLASS Polyether engineering thermoplastics

STRUCTURE



MAJOR APPLICATIONS Automotive, business machine, and electrical/electronics industries. PPO is mainly used to manufacture blends with high-impact polystyrene (HIPS). PPO/nylon, PPO/PBT, and PPO/polyolefin blends are also available on the market. PPO based materials rank first in terms of total consumption among blends based on engineering resins such as nylon, polycarbonate (PC), polyacetal, and reinforced terephthalate polyesters (PET and PBT).[(1)]

PROPERTIES OF SPECIAL INTEREST Amorphous and relatively nonpolar. Low moisture absorption, good strength, and high heat-resistance. Excellent compatibility with other polymers for blending. Pure PPO resin cannot be easily processed at temperatures above its glass transition temperature because of poor melt flow.

PREPARATIVE TECHNIQUES Prepared by oxidative C–O coupling polymerization of 2,6-dimethylphenol in an aromatic solvent at room temperature in the presence of a catalyst.[(2–5)] Generally, the catalyst is a copper and diamine complex.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight of repeat unit	$g\,mol^{-1}$	–	120.15	(1–5)
Typical molecular weight range of polymer	$g\,mol^{-1}$	Pyridine solvent	$2–3 \times 10^4$	(3)
		Nitrobenzene-pyridine solvent	$\sim 1 \times 10^5$	
		Commercial sample, Cu-diamine catalyst	3.72×10^4 (M_w)	
Typical polydispersity index (M_w/M_n)	–	Commercial sample, Cu-diamine catalyst	2.01	(6)
NMR	–	^{1}H-NMR ($CDCl_3$)		(7)
		^{13}C-NMR ($CDCl_3$)		(8)
		Analysis of hydroxyl end groups and molecular weight by ^{31}P-NMR		(9)
Thermal expansion coefficients	K^{-1}	–	5.2×10^{-5}	(10)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Compressibility coefficients	bar^{-1}	—	2.0×10^{-5}	(6)
Density (amorphous)	$g\,cm^{-3}$	296 K Melt	1.06 0.958	(6)
Solvents	Toluene, benzene, halogenated hydrocarbons			(6)
Nonsolvents	Acetone, alcohols, tetrahydrofuran			(6)
Solubility parameter	$(MPa)^{1/2}$	—	9.5–10.21	(11)
Theta temperature Θ	K	Methylene chloride	342.4	(12)
Interaction parameter χ				(13)

Second virial coefficient[14]

Solvent	$M_w \times 103^{-3}$ $(g\,mol^{-1})$	Temp. (K)	$A_2 \times 10^4$ $(mol\,cm^3\,g^{-2})$
Toluene	111	298	9.4
Benzene	130	298	11.1
Xylene	106	298	8.8
Chloroform	130	298	14.1
Dioxan	85	358	2.0

Mark-Houwink parameters: *K* and *a*

Solvent	Temp. (K)	$M_w \times 10^{-3}$ $(g\,mol^{-1})$	$K \times 10^2$ $(ml\,g^{-1})$	*a*	Reference
Toluene	298	26.5–415	2.85	0.68 ± 0.02	(15)
Chlorobenzene	298	26.5–415	3.78	0.66 ± 0.02	(15)
Chloroform	298	26.5–415	4.83	0.64 ± 0.02	(15)
Benzene	298	39.7–164	2.60	0.69	(14)
Carbon tetrachloride	298	39.7–164	7.44	0.58	(14)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Characteristic ratio $\langle r^2 \rangle_0 / nl^2$	—	Toluene, chlorobenzene Chloroform	4.74, 2.88 $(2\sigma^2)$	(15, 16)
Persistence length	Å	Benzene Carbon tetrachloride	0.84 0.86	(14)
Lattice	—	—	Monoclinic	(17)
Chain conformation	—	—	(4/1) helix	(17)

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Poly(2,6-dimethyl-1,4-phenylene oxide)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Unit cell dimensions	Å	α-Pinene solution	$a = 11.92$ $b = 17.10$	(17)
Unit cell angles	Degree	–	97 91.02	(17) (18)
Unit cell contents (number of repeat units)			6	(17)
Degree of crystallinity	%	Commercial sample (ΔH_f) As prepared (x-ray) Cooling from melt at $12\,K\,h^{-1}$ (ΔH_f) Exposure to 2-butanone (MEK)	40 25 0 ~ 30	(19) (19) (19) (20)
Heat of fusion (of repeat units)	$kJ\,mol^{-1}$	Methylene chloride 1-Chloronaphthalene DSC Toluene-polystyrene-PPO	5.88 3.77 1.80 ± 0.36 5.08	(12) (21) (19) (22)
Entropy of fusion (of repeat units)	$kJ\,K^{-1}\,mol^{-1}$	DSC	$(9.5 \pm 1.8) \times 10^{-3}$	(19)
Density (crystalline)	$g\,cm^{-3}$	–	1.16	(23)
Avrami exponent	–	Melt-crystallization	1.6	(24)
Glass transition temperature	K	DSC ($5\,K\,h^{-1}$) DSC (2.4×10^3 K,h^{-1})	498 480	(19) (25)
Melting point	K	DSC ($5\,K\,h^{-1}$) DSC (2.4×10^3 ,$K\,h^{-1}$)	535 540	(29) (25)
Heat capacity	$kJ\,K^{-1}\,mol^{-1}$	400–482 K 482–570 K	$C_p = (0.3428T + 53.86) \times 10^{-3}$ $C_p = (0.2279T + 141.09) \times 10^{-3}$	(26)
Deflection temperature	K	–	452	(27)
Polymers with which compatible		Polystyrene Poly(*p*-methylstyrene) Poly(α-methylstyrene) Poly(2-methyl-6-phenyl-1,4-phenylene ether) Poly(2-methyl-6-benzyl-1,4-phenylene ether) Brominated poly(2,6-dimethylphenylene ether)		(28) (29) (30) (31) (32) (33)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile modulus	MPa	ASTM D638		(10)
		296 K	2,690	
		366 K	2,480	
Shear modulus	MPa	ASTM D638		(10)
		296 K	2,690	
		366 K	2,480	
Tensile strength	MPa	ASTM D638		(10)
		296 K	80	
		366 K	55	
Maximum extensibility $(L/L_0)_r$	%	ASTM D638		(10)
		296 K	20–40	
		366 K	30–70	
Flexural modulus	MPa	ASTM D790		(10)
		256 K	2,650	
		296 K	2,590	
		366 K	2,480	
Flexural strength	MPa	ASTM D790		(10)
		263 K	2,650	
		296 K	2,590	
		366 K	2,480	
Impact strength	$J\,m^{-1}$	ASTM D256		(10)
		233 K, notched	53	
		296 K, notched	64	
		366 K, notched	91	
		Unnotched	>2000	
Hardness	—	Rockwell hardness	M78	(10)
Shear stress	MPa	ASTM D732	76	(10)
Important patents	U.S.P. 3,306,874 (1967), A. S. Hay (to General Electric Co.) U.S.P. 3,383,435 (1968), E. P. Cizek (to General Electric Co.)			

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Poly(dimethylsiloxane)

ALEX C. M. KUO

ACRONYM, ALTERNATE NAMES, TRADE NAMES PDMS; poly[oxy(dimethylsilylene)]; dimethicone; methylsilicone oil; Dow Corning® 200 fluid; Wacker SWS101 fluid; Baysilone® M fluid

CLASS Polysiloxanes; di-methyl silicones and siloxanes

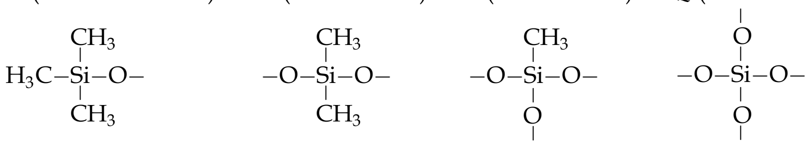
STRUCTURE $-[(CH_3)_2Si{-}O-]_n$

MAJOR APPLICATIONS Release agents, rubber molds, sealants and gaskets, surfactants, water repellents, adhesives, foam control agents, biomedical devices, personal care and cosmetics, dielectric encapsulation, glass sizing agents, greases, hydraulic fluids, heat transfer fluids, lubricants, fuser oil, masonry protectants, process aids.

PROPERTIES OF SPECIAL INTEREST Thermal stability, low temperature performance and minimal temperature effect. Good resistance to UV radiation. Excellent release properties and surface activity. High permeability to gases. Good damping behavior, antifriction and lubricity. Hydrophobic and physiological inertness. Shear stability, weak intermolecular forces, and excellent dielectric strength. Low volatility at high molecular weight, and high volatility at low molecular weight.

Shorthand notation for siloxane polymer units

Formula:	$(CH_3)_3SiO_{0.5}$	$(CH_3)_2SiO$	$(CH_3)SiO_{1.5}$	SiO_2
MDTQ formula:	M (monofunctional)	D (difunctional)	T (trifunctional)	Q (tetrafunctional)



End-group and structure of certain dimethylsiloxanes

End group	Structure	MDTQ formula	CAS Reg. No.
Methyl	$(CH_3)_3Si{-}O{-}[(CH_3)_2Si{-}O-]_nSi(CH_3)_3$	MD_nM	9016-00-6; 63148-62-9
Hydroxyl	$HO{-}(CH_3)_2Si{-}O{-}[(CH_3)_2Si{-}O-]_nSi(CH_3)_2{-}OH$	$M^{OH}D_nM^{OH}$	70131-67-8
Vinyl	$CH_2{=}CH{-}(CH_3)_2Si{-}O{-}[(CH_3)_2Si{-}O-]_nSi(CH_3)_2{-}CH{=}CH_2$	$M^{vi}D_nM^{vi}$	68083-19-2
Hydrogen	$H{-}(CH_3)_2Si{-}O{-}[(CH_3)_2Si{-}O-]_nSi(CH_3)_2{-}H$	$M^HD_nM^H$	70900-21-9
None	$[(CH_3)_2Si{-}O-]_3$; cyclic trimer	D_3	541-05-9
Methyl	$[(CH_3)_2Si{-}O-]_3SiH$	M_3T^H	1873-89-8

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Product form and properties[1]

Form	Structure and properties
Fluids	Linear polymer. Liquid at low molecular weights and solid gum at high molecular weights
Elastomers	Cross-linked solids. Reinforcement necessary for property performance
Resins	Highly branched cross-linked solids or fluids

Branched polymers[1]

Silicone resins and rubbers are cross-linked polymers with branched polymer chains containing M (monofunctional), D (difunctional), T (trifunctional), and Q (tetrafunctional) units. Slightly branched polymers made from D, T, and Q structures have lower bulk viscosity and intrinsic viscosity than linear polymers of the same average molecular weight.

Infrared characteristic absorption[2,3]

Group	Absorption, wave number (cm^{-1})
$-Si(CH_3)_2-O-Si(CH_3)_2-$	2,905–2,960; 1,020; 1,090
$Si(CH_3)_3$	2,905–2,960; 1,250; 840; 765
$Si(CH_3)_2$	2,905–2,960; 1,260; 855; 805
$Si-CH_3$	2,905–2,960; 1,245–1,275; 760–845
$Si-H$	2,100–2,300; 760–910
$Si-OH$	3,695; 3,200–3,400; 810–960
$Si-CH=CH_2$	1,590–1,610; 1,410; 990–1,020; 940–980

^{29}Si Nuclear magnetic resonance spectroscopy for typical structural building units in dimethylsiloxanes[4,5]

Structure	MDTQ formula*	Chemical shifts (ppm down-field from TMS)
$-O-Si(CH_3)_3$	M	6.6–7.3
$-Si(CH_3)_2-(C_6H_5)$	M^{ph}	−1
$-Si(CH_3)_2-CH=CH_2$	M^{vi}	−4
$-Si(CH_3)_2-H$	M^{H}	−7
$-Si(CH_3)_2-OH$	M^{OH}	−12
$-[O-Si(CH_3)_2-]$	D	−19 to −23
$[O-Si(CH_3)_2-]_3$	D_3	−9.1
$[O-Si(CH_3)_2-]_4$	D_4	−19.5
$(-O_{0.5}-)_3Si-CH_3$	T	−63 to −68
$(-O_{0.5}-)_4Si$	Q	−105 to −115

*See note above for ''Branched polymers.''

X-ray photoelectron spectroscopy elemental analysis[6]

Element identification	Binding energy	Atomic composition
Si-2p	102.6	25.0
C-1s	285.0	50.0
O-1s	532.6	25.0

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Preparative techniques

Polymerization process	Monomers	Major catalysts	Reference
Hydrolysis	Dichlorodimethylsilane and dialkoxydimethylsilane	Acids, alkalies, and polychlorophosphazenes	(1, 7, 8)
Condensation	Oligomeric dimethylsiloxane-diol	H_2SO_4, HCl, tin dicarboxylates, hydroxides of alkali metals or zeolite	(7, 9–11)
Anionic	Cyclic dimethylsiloxanes	Hydroxides, silanolates and alcoholates of alkali metals, quaternary ammonium or phosphonium bases	(7, 9, 12–14)
Cationic	Cyclic dimethylsiloxanes	Strong protic acids (H_2SO_4 and CF_3SO_3H)	(7, 9, 14, 15)
Emulsion	Silanol ended oligomer or cyclic dimethylsiloxanes	Sodium silicate, tin dicarboxylates acid salt hydroxides of alkali metals	(16–18)
Radiation	Cyclic dimethylsiloxanes	γ (^{60}Co)	(9)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Enthalpy of polymerization $-\Delta H_p$	$kJ\,mol^{-1}$	D_3 at 25°C	2.79	(19)
		D_3 at 77°C	23.4	
		D_4 at 25°C	−6.4	
		D_4 at 77°C	−13.4	
Entropy of polymerization ΔS_p	$J\,K^{-1}\,mol^{-1}$	D_3 at 25°C	51.0	(19)
		D_3 at 77°C	−3.03	
		D_4 at 25°C	194.4	
		D_4 at 77°C	190.0	
Ceiling temperature	K	PDMS in toluene with 0.22 $g\,ml^{-1}$	383	(20)
Solvents	Benzene, toluene, xylene, diethyl ether, chloroform, carbon tetrachloride, ethyl acetate, butanone, perchloroethylene, kerosene			(21)
Partially soluble solvents	Acetone, ethanol, isopropanol, butanol, dioxane, ethyl phenyl ether			(21)
Nonsolvents	Water, methanol, cyclohexanol, ethylene glycol, 2-ethoxy ethanol, dimethyl phthalate, aniline, 2-ethoxyethanol, 2-(2-ethoxyethoxy)ethanol, bromobenzene			(21)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Solubility parameter δ	$(MPa)^{1/2}$	Average range	14.9–15.59	(22)
		PDMS (100–60,000 cs)	15.1	(23)
		Static vapor sorption for PDMS ($M_n = 89{,}000$)	15.0	(24)
		Gas chromatography method for PDMS ($M_n = 2{,}410$–$218{,}000$) at 25°C	15.1	(25)
		Gas chromatography method for PDMS ($M_n = 2{,}410$–$218{,}000$) at 90°C	13.4	(25)
Theta temperature Θ	K	Bromobenzene	351.7	(26)
		Bromocyclohexane	302	(26)
		Bromocyclohexane	300.6	(27)
		Ethyl iodide	275.1	(26)
		Ethyl phenyl ether	362.5	(26)
		Ethyl phenyl ether	356	(28)
		Butanone	293	(29)
Second virial coefficient A_2	$mol\,cm^3\,g^{-2}$	PDMS		
		In toluene at 27°C	4.5×10^{-4}	(27)
		In benzene at 27°C	2.95×10^{-4}	(27)
		In chlorobenzene at 30°C	10.4×10^{-5}	(27)
		In bromobenzene at 40°C	3.0×10^{-5}	(26)
		In bromocyclohexane at 36.5°C	3.62×10^{-5}	(27)
		In bromocyclohexane at 47.2°C	6.57×10^{-5}	(27)
		In bromocyclohexane at 56.2°C	9.54×10^{-5}	(27)
		In benzene at 20°C	2.1×10^{-4}	(29)
		In benzene at 20°C	1.84×10^{-4}	(29)

Mark-Houwink parameters: *K* and *a*

Solvents	Temp. (°C)	$K \times 10^3$ ($ml\,g^{-1}$)	*a*	Reference
Butanone	20	81.5	0.5	(28)
Butanone	20	89	0.5	(30)
Butanone	20	78.3	0.5	(29)
Ethyl phenyl ether	83	77	0.5	(28)
Ethyl phenyl ether	89.5	73	0.5	(26)
Toluene	25	20	0.66	(31)
Toluene	25	8.28	0.72	(29)
Toluene	25	11	0.92	(30)
Benzene	20	12	0.68	(29)
Mixture of C_8F_{18} and $C_2Cl_4F_2$ (1:2)	22.5	105.7	0.5	(29)
Bromobenzene	78.7	76	0.5	(26)
Ethyl iodide	2.1	70	0.5	(26)
Bromocyclohexane	29	74	0.5	(26)

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Characteristic ratio $C_\infty = \langle r^2 \rangle_0 / nl^2$	—	Mixture of C_8F_{18} and $C_2Cl_4F_2$ (1:2) at 22.5°C		7.7	(29)
		Butanone at 20°C		6.3	(29)
		Calculation based on Ising lattice method ($l = 1.64$ Å, $\theta_1 = 110°$, $\theta_2 = 143°$)		3.32–5.28	(32)
Root-mean-square end-to-end chain length $(\langle r^2 \rangle_0 / M)^{1/2}$	nm $mol^{1/2}$ $g^{-1/2}$	PDMS in various theta solvents		2.5×10^{-2}	(26)
		PDMS in butanone at 20°C		7.30×10^{-2}	(28)
		Free rotation value calculated at 20°C for $l = 1.65$ Å, $\theta_1 = 110°$, $\theta_2 = 130°$		4.56×10^{-2}	(28)
		Free rotation value calculated at 20°C for $l = 1.65$ Å, $\theta_1 = 110°$, $\theta_2 = 160°$		5.30×10^{-2}	(28)
Root-mean-square radius of gyration $R_g = \langle s^2 \rangle_z^{1/2}$	Å	Blend of PDMS and preduterated PDMS (M_n = 3,000–25,000)		41	(33)
		PDMS in benzene-d_6			
		$M_z = 4,990$		18.6	(34)
		$M_z = 8,670$		25.2	(34)
		$M_z = 12,890$		33.8	(34)
		$M_z = 20,880$		49.4	(34)
		Network prepared by PDMS and preduterated PDMS		39	(33)
Z-average square radius of gyration $\langle s^2 \rangle_{z,linea} / \langle s^2 \rangle_{z,ring}$	—	Linear and cyclic PDMS in diluted benzene-d_6		1.9 ± 0.2	(34)
Interaction parameter of PMDS in organic solvents χ_{12}	—	Organic solvent	Conditions		
		Pentane	Swelling at 25°C	0.43	(35)
		Toluene	Swelling at 25°C	0.465	(35)
		Nitrobenzene	Swelling at 25°C	2.2	(35)
		Ethyl ether	Swelling at 25°C	0.43	(35)
		Cyclohexane	Swelling at 25°C	0.44	(35)
		Hexane	Swelling at 25°C	0.40	(35)
		Carbon tetrachloride	Swelling at 25°C	0.45	(35)
		Ethyl iodide	Swelling at 25°C	0.58	(35)
		Dioxane	Swelling at 25°C	0.61	(35)
		2,3-dimethylpentane	Swelling at 25°C	0.392	(36)
		2,2,4-trimethylpentane	Swelling at 25°C	0.38	(36)
		Chlorobenzene	Osmotic measurement at 20°C	0.477	(37)
		Cyclohexane	Osmotic measurement at 25°C	0.429	(37)
		Benzene	Osmotic measurement at 25°C	0.481	(37)

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
		Organic solvent	Conditions		
		Pentane	Gas chromatography at 100°C	0.311	(38)
		Toluene	Gas chromatography at 100°C	0.594	(38)
		Cyclohexane	Gas chromatography at 100°C	0.351	(38)
		Hexane	Gas chromatography at 100°C	0.296	(38)
		Chloroform	Gas chromatography at 100°C	0.60	(38)
		Benzene	Gas chromatography at 100°C	0.577	(38)
		Chlorobenzene	Gas chromatography at 100°C	0.764	(38)
		Dioxane	Gas chromatography at 100°C	1.064	(38)
		n-Butanol	Gas chromatography at 100°C	1.908	(38)
		Ethanol	Gas chromatography at 100°C	2.571	(38)

Interaction parameter χ_{12}

Materials/condition	Temp. (K)	Method	χ_{12}	Reference
PDMS network/PDMS ($M = 422–875$)	298	Swelling	0.19–0.25	(35)
PDMS network/PDMS ($M = 700–26{,}400$)	298	Swelling	−0.017 to 0.006	(39)
PDMS network/D_5	298	Swelling	0.247	(40)
PDMS/D_4	298	Osmotic measurement	0.298	(41)
PDMS network/$MD_3^{ph}M$	298	Swelling	0.345	(42)
PDMS network/$MD_2^{ph}M$	298	Swelling	0.438	(42)
PDMS network/$MD^{ph}M$	298	Swelling	0.356	(42)
$MD_{13}M/MD_{28}^{ph}M$	458	Light scattering	0.112	(43)
$MD_{13}M/MD_{23}^{ph}M$	518	Light scattering	0.122	(43)
$M^{OH}D_{15}M^{OH}/MD_{23}^{ph}M$	446	Light scattering	0.111	(44)
$MD_{13}M/D_4^{ph}$ cycloisomers	360–371	Light scattering	0.300	(40)
PDMS/polyethylmethylsiloxane ($M_n = 30{,}300$)	332.5	Light scattering	0.00664–0.0077	(45)
PDMS/poly(ethylene oxide)	343–373	Gas chromatography	0.4–1.1	(46)

Parameters for the equation of state

PDMS	Method	T^* (K)	$V_{sp}{}^*$ (cm^3 g^{-1})	P^* (MPa)	Reference
$M_v = 1 \times 10^5$	Flory-Orwoll and Vrij theory at 25°C	5,528	0.8395	341	(47)
$M_n = 162.4$	Flory-Orwoll and Vrij theory at 25°C	4,468	0.9995	325.3	(48)
$M_n = 340$	Modified Flory-Orwoll and Vrij theory at 40–73°C	3,726.5	0.94877	373.9	(49)
$M_n = 958$	Flory-Orwoll and Vrij theory at 25°C	5,288	0.8694	313.3	(48)
$M_n = 7,860$	Flory-Orwoll and Vrij theory at 25°C	5,554	0.8403	311.5	(48)
$M_n = 187,000$	Modified Flory-Orwoll and Vrij theory at 42–93°C	4,386.7	0.88085	382.6	(49)
$M_n = 47,200$	Ising fluid model at 25–70°C	476	0.9058	302	(50)

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Morphology in multiphase systems

System A/B	Microstructure	Architecture	Reference
Poly(butadiene)/PDMS	Cylinders/spheres	A-B diblock	(51)
Poly(styrene)/PDMS	Spheres/lamellae/cylinders	A-B diblock	(52)
Poly(diphenylsiloxane)/PDMS	Lamellae	A-B-A triblock or star-block	(53)
Poly(methyl styrene)/PDMS	Spheres/lamellae	A-B diblock and A-B-A triblock	(54)
Poly(ethylene oxide)/PDMS	Lamellae/cylinders	B-A-B triblock	(46)
Poly(methyl methacrylate)/ PDMS	Spheres/cylinders	A-g-B graft	(55)

Properties of trimethylsiloxy terminated polydimethylsiloxane vs. viscosity[23,56]

Properties	Units	PDMS viscosity at 25°C (cs)						
		0.65	2.0	10	100	1,000	12,500	60,000
Molecular weight (estimated)	$g\ mol^{-1}$	162	410	1,250	5,970	28,000	67,700	116,500
Flash point	K	269.7	352	484	>599	>599	>599	>599
Pour point	K	205	173	173	208	223	227	232
Freezing point	K	205	189	—	—	—	227	—
Specific gravity at 25°C	—	0.760	0.872	0.935	0.964	0.970	0.974	0.977
Viscosity temperature coefficient $[1 - (\eta_{372K}/\eta_{311K})]$	—	0.31	0.48	0.56	0.60	0.61	0.61	0.61

PROPERTY	UNITS	CONDITIONS	VALUE*	REFERENCE
Density ρ	$g\ cm^{-3}$	PDMS (1,000–12,500 cs)	0.970	(56)
ρ vs. temperature	—	PDMS ($M_v = 1 \times 10^5$) from 20–207°C	$\rho = 0.9919 - (8.925 \times 10^{-4})t + (2.65 \times 10^{-7})t^2 - (3.0 \times 10^{-11})t^3$	(47)
Specific volume ν_{sp}	$cm^3\ g^{-1}$	From 20–90°C	$\nu_{sp} = 1.0265 + (9.7 \times 10^{-4})(t - 20)$	(57)
ν_{sp} vs. temperature	—	From 90–170°C	$\nu_{sp} = 1.0944 + (10.3 \times 10^{-4})(t - 90)$	(57)
Thermal expansion coefficient α	K^{-1}	PDMS ($M_v = 1 \times 10^5$) at 25°C	9.07×10^{-4}	(47)
		PDMS (from 100–60,000 cs)	9.6×10^{-4}	(23)
		PDMS ($M = 1.5 \times 10^4$) at 30°C	9.0×10^{-4}	(58)
α vs. temperature	—	PDMS ($M_v = 1 \times 10^5$) from 20–207°C	$\alpha = 0.90 \times 10^{-3} + (2.76 \times 10^{-7})t + (1.0 \times 10^{-10})t^2$	(47)
Thermal pressure coefficient, γ, vs. temperature	$bar\ K^{-1}$	PDMS ($M_v = 1 \times 10^5$) from 24–161°C	$\gamma = 8.71 + (4.74 \times 10^{-2})t + (9.3 \times 10^{-5})t^2$	(47)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Water solubility	ppm	MDM at 296 K, nonturbulent measurement	3.45×10^{-2}	(59)
		MD_3M at 296 K, nonturbulent measurement	7.0×10^{-5}	(59)
		PDMS ($M = 1{,}200$) at 298 K, water elution measurement	1.6	(60)
		PDMS ($M = 6{,}000$) at 298 K, water elution measurement	0.56	(60)
		PDMS ($M = 25{,}000$) at 298 K, water elution measurement	0.17	(60)
		PDMS ($M = 56{,}000$) at 298 K, water elution measurement	0.076	(60)

Compressibility[61]

Pressure (kgf cm^{-2})	Viscosity of PDMS (cs)						
	0.65	1	2	100	350	1,000	12,500
	Volume reduction (%)						
0	0	0	0	0	0	0	0
500	6.34	5.36	4.85	4.49	4.47	4.58	4.46
1,000	10.04	8.84	8.21	–	7.42	7.36	7.29
25,000	16.33	15.08	14.34	12.71	12.78	12.74	12.53
50,000	Gel	20.66	20.07	17.43	17.96	17.87	17.71
30,000	–	34.57	34.56	–	32.94	31.31	31.25

X-ray diffraction pattern[62]

Condition	2θ	Reflection
PDMS rubber at −50°C for 6 h	11°40′ (amorphous halo)	110 + 001
	19°30′	110 + 020
	23°20′	021 + 112

Unit cell dimensions[63]

Lattice	Monomer per unit cell	Unit cell dimension (Å)			Cell angle (degrees)			Theoretical density (g cm^{-3})	
		a	*b*	*c*	α	β	γ	Crystal	Amorphous
Monoclinic	6	13.0	8.3	7.75	90	60	90	1.07	0.98

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Crystalline state properties

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Si–C bond length	Å	$[(CH_3)_2SiO-]_4$ at $-50^\circ C$	1.92	(64)
Si–O bond length	Å	$[(CH_3)_2SiO-]_4$ at $-50^\circ C$	1.65	(65)
Si–C bond energy	$kJ\,mol^{-1}$	–	326	(65)
Si–O bond energy	$kJ\,mol^{-1}$	–	443	(65)
O–Si–O bond angle	Degree	$[(CH_3)_2SiO-]_4$ at $-50^\circ C$	109	(64)
		Conformation analysis	112	(66)
Si–O–Si bond angle	Degree	X-ray diffraction analysis	140 ± 10	(63)
		Conformation analysis for hexamethyldisloxane	145–150	(67)
		$[(CH_3)_2SiO-]_4$ at $-50^\circ C$	142.5	(64)
C–Si–C bond angle	Degree	$[(CH_3)_2SiO-]_4$ at $-50^\circ C$	106	(64)
Degree of crystallinity α	%	X-ray measurement for 17% silica filled PDMS rubber at $-60^\circ C$	42	(68)
		X-ray measurement for 17% silica filled PDMS rubber at -80°C	59	(68)
		DSC measurement for PDMS ($M_n = 1.11 \times 10^5$) at T_g using a cooling rate = $10\,K\,min^{-1}$	58.8	(69)
		Calorimeteric measurement for PDMS ($M \sim 6 \times 10^5$) at T_g	67	(19)
		DSC measurement for PDMS at T_g using a cooling rate = $2.1\,K\,min^{-1}$	79	(70)

Avrami parameters

Conditions	Crystallization temp., T_c (°C)	$k \times 10^3$	n	$\tau_{0.5}$ (min)	Reference
Isothermal crystallization of PDMS ($M = 4 \times 10^5$)	−55.6	1.905	2.19	15	(62)
	−58.0	5.75	2.08	8	(62)
	−57.5	7.0	2.2	9	(71)
	−60.5	120	1.75	2.5	(71)
Isothermal crystallization of PDMS ($M = 1 \times 10^5$)	−60.5	1.0	2.5	13.5	(71)
	−65.0	7.35	2.2	8.2	(71)
	−71.0	23	2.25	4.8	(71)
NMR measurement for PDMS ($M_n = 7.4 \times 10^5$)	−58.8	–	3.1	–	(72)

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Glass transition temperature T_g	K	Measured by DSC	150		(70)
			123.3–149.9		(73)
Melting point T_m	K	Measured by DSC	T_{m1}	T_{m2}	
			226–232	236	(70)
			217.8–228.3	235.3–235.6	(73)
Cold crystallization temperature T_c	K	Measured by DSC	173–183		(70)
			181.4–196.8		(73)
Enthalpy of fusion ΔH_u	$kJ\,mol^{-1}$	Calculation by melting temperature depression of PDMS in toluene solution	1.36		(70)
		Calorimeteric measurement for a PDMS ($M \sim 6 \times 10^5$) with 67% crystallinity	3.04		(19)
Entropy of fusion ΔS	$kJ\,K^{-1}\,mol^{-1}$	Calculation by melting temperature depression of PDMS in toluene solution	5.78×10^{-3}		(70)
		Calorimeter measurement for a PDMS ($M \sim 6 \times 10^5$) with 67% crystallinity	12.46×10^{-3}		(19)
Specific heat C_p	$kJ\,kg^{-1}\,K^{-1}$	PDMS (2–1,000 cs)	1.35–1.51		(56)
		PDMS (350 cs) at 298 K	1.464		(23)
		PDMS (1,000 cs) at 298 K	1.461		(23)
		PDMS ($M = 400{,}000$)	1.552		(23)
Specific heat, C_p, effect of temperature	–	PDMS ($M_n = 1.11 \times 10^5$) at:			(69)
		120 K	0.66		
		140 K	0.824		
		250 K	1.439		
		300 K	1.532		
		350 K	1.625		
Bulk viscosity-molecular weight relationship	cs	PDMS ($M_n > 2{,}500$) at 25°C	$\log \eta = 1.00 + 0.0123M^{0.5}$		(31)
Energy of vaporization E_{vap}	$kJ\,mol^{-1}$	MD_9M	90.45		(74)
		MD_8M	83.75		

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Energy of activation for viscous flow E_{visc}	$kJ\,mol^{-1}$	MD_9M	13.74	(74)
		PDMS ($M = 4.7 \times 10^3$ to 4.8×10^5)	14.6	(75)
Critical molecular weight for entanglement M_c	$g\,mol^{-1}$	Linear PDMS	21,000	(76)
		Linear PDMS	29,000	(31, 77)
		Linear PDMS	30,000	(75)
		Linear PDMS	33,000	(78)
		Trifunctional branched PDMS	98,000	(78)
		Tetrafunctional branched PDMS	110,000	(78)
Color	APHA	PDMS (Dow Corning 200 fluids)	5	(23)

Monolayer properties of force vs. area isotherm for PDMS on water surface[79]

Property	Units	Material	Value
Area per monomer unit A_0	$Å^2$	$MD_{14}M$	22
Film pressure, F, at 7 Å2	$mN\,m^{-1}$	$MD_{14}M$	10.2
Surface electrostatic potential difference, ΔV, at 7 $Å^2$	mV	$MD_{14}M$	150
Apparent dipole moment per mole per monolayer, μ_p, at 7 $Å^2$	mD	$MD_{14}M$	30

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Water contact angle θ	Degrees	PDMS (500 cs) film on soda-lime glass after 15 min treatment		
		At 25°C	54	(80)
		At 100°C	70	(80)
		At 200°C	102	(80)
		At 300°C	110	(80)
		At 400°C	103	(80)
		At 500°C	85	(80)
		At 525°C	0	(80)
		PDMS films end-grafted onto silicone wafer	112–117.5	(81)
		PDMS fluid, cross-linked PDMS paper coating, and unfilled PDMS elastomer	95–113	(82)
Methylene iodide contact angle θ	Degrees	PDMS fluid, cross-linked PDMS paper coating, and unfilled PDMS elastomer	67–77	(82)
n-Hexadecane contact angle θ	Degrees	Surface of cross-linked PDMS sheet	40	(83)
Perfluorodecalin contact angle θ	Degrees	PDMS elastomer vs. perfluorocarbon monolayer on mica surface	37	(84)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Critical surface tension γ	$mN\ m^{-1}$	Silica filled PDMS rubber at 20°C	20–23	(85)
		Dimethylsiloxane dimer at 20°C	15.7	(86)
		Dimethylsiloxane tetramer at 20°C	17.60	(86)
		Dimethylsiloxane heptamer at 20°C	18.60	(86)
		Dimethylsiloxane dodecamer at 20°C	19.56	(86)
		PDMS (35 cs) at 20°C	19.9	(86)
		PDMS (70 cs) at 20°C	20.3	(86)
		PDMS (100 cs) at 25°C	20.9	(23)
		PDMS (1,000 cs) at 25°C	21.2	(23)
		PDMS (12,500 cs) at 25°C	21.5	(23)
		PDMS (10^6 and 6×10^4 cs) at 20°C	20.4	(57)
		PDMS (10^6 and 6×10^4 cs) at 150°C	13.6	(57)
		PDMS (6×10^4 cs) at 180°C	12.1	(87)
Surface tension vs. M_n	$mN\,m^{-1}$	PDMS at 24°C	$\gamma^{-0.25} = (21.06)^{-0.25} + 8.486/M_n$	(87)
Temperature coefficient of surface tension $-d\gamma/dT$	$mN\,m^{-1}\,K^{-1}$	PDMS (10^6, 6×10^4 cs) at 150°C	0.048	(57)
		PDMS (35 cs) at 20°C	0.067	(86)
Interfacial tension against water γ_{1w}	$mN\,m^{-1}$	PDMS (0.65 cs) at 20°C	39.9	(86)
		PDMS (1.0 cs) at 20°C	42.5	
		PDMS (5.0 cs) at 20°C	42.2	
		PDMS (35 cs) at 20°C	43.1	
Polarity x^p		Form interfacial tension of PDMS (6×10^4 cs)	0.042	(87)
Friction force (interfacial shear strength)	$N\,m^{-2}$	PDMS elastomer vs. fluorocarbon monolayer on mica surface	$21.4(\pm 0.7) \times 10^4$	(88)
		PDMS elastomer vs. hydrocarbon monolayer on mica surface	$4.6(\pm 0.2) \times 10^4$	
Surface shear viscosity	$\mu N\,sm^{-1}$	PDMS (M = 500–105,000)	~1	(89)

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Interfacial tension of polymer pairs

Polymer pair	γ_{12}, (mN m^{-1})	$-d\gamma_{12}/dT$, (mN m^{-1} K^{-1})	Reference
PDMS/polypropylene	3.2 at 20°C	0.002	(90)
PDMS/poly(*t*-butyl methacrylate)	3.6 at 20°C	0.0025	(91)
PDMS/poly(isobutene)	4.9 at 20°C	0.006	(92)
PDMS/poly(isobutylene)	3.9 at 20°C	0.016	(93)
PDMS/polybutadiene	4.15 at 25°C	0.00865	(94)
PDMS/poly(*n*-butyl methacrylate)	4.2 at 20°C	0.0038	(91)
PDMS/polyethylene, branch	5.3 at 20°C	0.002	(89, 92)
PDMS/polystyrene	6.1 at 20°C	~0	(92)
PDMS/poly(oxytetramethylene)	6.4 at 20°C	0.0012	(91)
PDMS/polychloroprene	7.1 at 20°C	0.0050	(91)
PDMS/poly(vinyl acetate)	8.4 at 20°C	0.0081	(91, 93)
PDMS/polyethylene	5.08 at 150°C	0.0016	(95)
PDMS/poly(vinyl acetate)	7.43 at 150°C	0.0087	(95)
PDMS/poly(oxyethylene)	9.85 at 150°C	0.0078	(95)
PDMS/poly(tetrahydrofuran)	6.26 at 150°C	0.0004	(95)

Gas permeability from PDMS membranes filled with 33% silica (cm^3(STP) cm (s cm^2 cm Hg)$^{-1}$)[96]

Gas	$Pr \times 10^9$	Gas	$Pr \times 10^9$	Gas	$Pr \times 10^9$
H_2	65	N_2O	435	*n*-C_6H_{14}	940
He	35	NO_2	760	*n*-C_8H_{18}	860
NH_3	590	SO_2	1500	*n*-$C_{10}H_{22}$	430
H_2O	3600	CS_2	9000	HCHO	1110
CO	34	CH_4	95	CH_3OH	1390
N_2	28	C_2H_6	250	$COCl_2$	1500
NO	60	C_2H_4	135	Acetone	586
O_2	60	C_2H_2	2640	Pyridine	1910
H_2S	1000	C_3H_8	410	Benzene	1080
Ar	60	*n*-C_4H^{10}	900	Phenol	2100
CO_2	325	*n*-C_5H_{12}	2000	Toluene	913

Temperature effect of oxygen permeability and solubility from PDMS membrane[96]

Temp. (°C)	$Pr \times 10^9$ (cm^3(STP) cm (s cm^2 cm Hg)$^{-1}$)	Solubility (ml g^{-1})
28	62	0.31
−40	20	0.39
−75	0.74	47

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Solubility of gases in PDMS at 25°C/760 mm Hg

Gas	Solubility (ml g^{-1})[61]	Solubility (ml g^{-1})[96]	Diffusion rate, $D \times 10^5$ ($cm^2\ s^{-1}$)[96]
He	0.010	0.045	60
Ar	0.301	0.33	14
Air	0.168	–	–
O_2	0.258	0.31	16
N_2	0.166	0.15	15
CO_2	1.497	2.2	11
CH_4	0.543	0.57	12.7
SF_6	0.996	–	–
C_3F_8	1.041	–	–
H_2	–	0.12	–
C_4H_{10}	–	15.0	25

Williams-Landel-Ferry (WLF) parameters measurement for trimethylsiloxy-terminated PDMS[133]

PDMS, M_n (g mol^{-1})	Reference temp. T_0 (K)	C_1	C_2 (K^{-1})	T_g, DSC (K)
10370	147	10.4	14.24	149.5
4160	145.5	14.22	23.84	149.3
2080	143.8	14.32	23.37	147.5
830	141.1	13.48	20.03	141.2
420	136.5	11.46	14.01	135.9

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Thermal conductivity	$W\ m^{-1}\ K^{-1}$	PDMS (100 cs) at 80°C	0.1511	(56)
		PDMS (1,000 cs) at 80°C	0.1566	(56)
		PDMS (12,500 cs) at 80°C	0.1520	(56)
		PDMS (1,000–60,000 cs) at 50°C	0.1591	(23)
		PDMS (12,500 cs) at 14.7°C	0.1678	(98)
Load-bearing capacity	kg	PDMS fluid	50–150	(1)
Lubricity	mm	Shell four ball test; wear scar, steel on steel; PDMS (100 cs) at 1 h/600 rpm/50 kg load/ambient temperature	1.91	(99)
		Shell four ball test; wear scar, steel on bronze; PDMS (100 cs) at 1 h/600 rpm/10 kg load/ambient temperature	2.0	
Speed of sound longitudinal velocity	$m\ s^{-1}$	PDMS (0.65 cs) at 30°C	837.2	(97)
		PDMS (50 cs) at 30°C	981.6	
		PDMS (100 cs) at 30°C	985.2	
		PDMS (1,000 cs) at 30°C	987.3	
		PDMS (1,000 cs) at 50.7°C	933.3	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Temperature coefficient of sound transmission	—	PDMS (0.65 cs) at 30°C	−3.8	(97)
		PDMS (50 cs) at 30°C	−2.7	
		PDMS (100 cs) at 30°C	−2.7	
		PDMS (1,000 cs) at 30°C	−2.6	
Anomalous longitudinal velocity due to phase transition effect	$m\,s^{-1}$	PDMS (200,000 cs) cooling at $T < 205$ K	1,850	(100)
		PDMS (200,000 cs) cooling at $T > 235$ K	1,200	

Dielectric properties of trimethylsiloxy terminated PDMS at various viscosity[23, 101]

Viscosity at 25°C (cs)	0.65	2.0	10	100	1,000	12,500	60,000
Dielectric constant, at 10^2–10^4 Hz	2.2	2.45	2.72	2.75	2.75	2.75	2.75
Dielectric strength at 25°C ($kV\,cm^{-1}$)	118	138	148	158	158	158	158
Volume resistivity at 25°C (ohm cm)	1.0×10^{14}	5.0×10^{14}	1.0×10^{15}	1.0×10^{15}	1.0×10^{15}	1.0×10^{15}	1.0×10^{15}

Dielectric data for PDMS (440 cs) at various temperatures[1]

Properties	Units	Sample	20°C	100°C	200°C
Dielectric constant ε	—	PDMS (440 cs)	2.8	2.5	2.3
Dissipation factor, $\tan\delta$ at 800 Hz	—	PDMS (440 cs)	1.2×10^{-4}	1.3×10^{-4}	1.5×10^{-4}
Volume resistivity	ohm cm	PDMS (440 cs)	4×10^{15}	6×10^{14}	1×10^{14}
Dielectric strength	$kV\,cm^{-1}$	PDMS (440 cs)	120	100	95

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Refractive index n_D^{25}	—	PDMS (0.65–10 cs) at 25°C	1.375–1.399	(101)
		PDMS (100–60,000 cs) at 25°C	1.4030–1.4036	
Diamagnetic susceptibility X_m	$cm^3\,g^{-1}$	PDMS (M = 1,200)	0.620×10^{-6}	(102)
		MD_5M	0.658×10^{-6}	(103)
		D_3 and D_4	0.632×10^{-6}	(103)
Verdet constant of magnetic rotary power	min $gauss^{-1}$ cm^{-1}	PDMS (0.65–1,000 cs) at 25°C and 5,893 Å	$(1.623–1.693) \times 10^{-2}$	(104)
Dipole moment μ	D	Hydroxy-terminated PDMS (M = 20,000) in cyclohexane at 25 °C	11.54	(105)
		Hydroxy-terminated PDMS (M = 70,230) in cyclohexane at 25 °C	21.48	
		Trimethylsiloxy-terminated PDMS (M = 78,500) in cyclohexane at 25 °C	22.24	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dipole moment per repeat unit $\mu/n^{1/2}$	D	Trimethylsiloxy-terminated PDMS in cyclohexane	0.697	(105)
		Hydroxy-terminated PDMS in cyclohexane	0.666	
Root-mean-square dipole moment ratio $\langle\mu^2\rangle_0/nm^2$	–	PDMS (DP = 194–2,076) undiluted at 25 °C	0.30	(106)
		PDMS (DP = 194–2,076) in cyclohexane at 25 °C	0.40	(106)
		PDMS (DP = 2–4,940) in cyclohexane at 25°C	0.29	(107)
True contact charge density	$nC\,cm^{-2}$	RTV silicone rubber under contact pressure ($1.2 \times 10^4\,N\,m^{-2}$)	-15 ± 5	(108)
Autoignition temperature (ASTM D 286-30)	K	PDMS (1 cs)	691	(21)
		PDMS (5 cs)	716	
		PDMS (10 cs)	725	
		PDMS (100 cs)	>763	
Limiting oxygen index (LOI)	%	PDMS silicone rubber	26–42	(109)
Arc resistance	s	PDMS silicone rubber	250	(109)
Corona resistance	kV	PDMS silicone rubber	40	(109)

Anisotropy of segments and monomer units of PDMS

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Optical configuration parameter Δa	cm^3	PDMS ($M = 1.8 \times 10^6$) in petroleum ether	0.96×10^{-25}	(110)
		Cross-linked PDMS at 20°C	4.5×10^{-25}	(111)
		Cross-linked PDMS at −60°C	0	(111)
		Cross-linked PDMS at 70°C	8.1×10^{-25}	(112)
		Cross-linked PDMS swelled in decalin at 70°C	5.1×10^{-25}	(112)
		Cross-linked PDMS swelled in cyclohexane at 70°C	3.8×10^{-25}	(112)
		Cross-linked PDMS swelled in CCl_4 at 70°C	1.8×10^{-25}	(112)
Stress-optical coefficient C	$m^2\,N^{-1}$	PDMS		
		At 200°C	1.35×10^{-10}	(113)
		At 22/25°C	$1.35/1.75 \times 10^{-10}$	(114)
		At 105/190°C	$1.9/2.65 \times 10^{-10}$	(114)

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Degradation behavior

End-group of PDMS	Depolymerization conditions	Activation energy ($kJ\,mol^{-1}$)	Reference
Trimethylsiloxy-terminated	Random scission thermal depolymerization at 420–480°C	176	(115)
Trimethylsiloxy-terminated	Thermal oxidation depolymerization at 350–420°C	126	(115)
Hydroxyl-terminated	Unzipping in vacuum at $T > 250$°C	35.6	(115)
Hydroxyl-terminated	0.01% NaOH or 0.01% H_2SO_4 catalyzed depolymerization at 170–300°C	58.6	(116)
Hydroxyl-terminated	Stress relaxation measurement in anhydrous argon at 150–260°C	95.4	(117)
Hydroxyl-terminated	0.01% KOH catalyzed reaction at 60–140°C	21.4	(118)
Trimethylsiloxy-terminated ^{14}C-PDMS	Degradation occurred in soil with $< 3\%$ moisture and formed volatilized dimethylsilane diol	—	(119)
Trimethylsiloxy-terminated ^{14}C-PDMS	No biodegradation was found in activated sewage sludge bacteria	—	(119)

Thermochemical parameters[118]

Viscosity of PDMS (cs)	Heat of gasification ($MJ\,kg^{-1}$)	Heat of combustion ($MJ\,kg^{-1}$)	Flame heat radiated to surface ($kW\,m^{-2}$)
0.65	0.327	36.1	—
2.0	0.492	30.0	—
10	3.0–3.6	26.8	26
10,000,000	3.0–3.6	26.8	26

Decomposition products[120]

Thermal decomposition products (100 cs PDMS)	% at 475°C	Thermal-oxidative decomposition product	% at 430°C (approximate)
D_3	45	Cyclic siloxanes	81
D_4	19	HCHO	13
D_5	5	CO_2	3
D_6	11	CO	2
D_7	7	CH_3OH	1.5
D_8	2	HCO_2H	0.2

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Fire parameters (cone calorimeter test)[118]

Samples	External heat flux ($kW\,m^{-2}$)	Peak rate of heat release ($kW\,m^{-2}$)	Specific extinction area ($m^2\,kg^{-1}$)
MM	30	2,800	–
MD_2M	60	2,200	–
MD_3M	60	1,750	–
MD_8M	60	750	–
10 cs PDMS	60	175	–
50 cs PDMS	60	140	600
6×10^5 cs PDMS	60	105	550
1×10^7 cs PDMS	60	95	550
Elastomers/silica filled	60	80-110	1,300–1,700

Ecotoxicity in aquatic compartment

Species	Materials	Result or hazard rating	Reference
Fresh water			
Salmo gairdneri	PDMS (350 cs) 25% in food for 28 days, followed by a 14-day observation period	No effect on behavior and growth with 10 mg PDMS $fish^{-1}\,day^{-1}$	(119)
Phoxinus phoxinus	PDMS (viscosity not specified)	LC_{40} – 8 days = 3,000 ($mg\,l^{-1}$)	(119)
Leuciscus idus	350 (Baysilone fluid M350)	LC_0 – 96 h = 200 ($mg\,l^{-1}$)	(121)
Sea water			
Pomatoschistus minutus, *Gasterosteus aculeatus*	PDMS (100, 350, and 12,500 cs)	No mortality 96 h at saturation	(119)
Pleuronectes platessa	PDMS (50 cs)	Toxicity – 96 h > 10,000 $mg\,l^{-1}$ at the surface of water (5 $mg\,l^{-1}$ in water)	(119)
Scorpaena porcus	PDMS (50 cs) 30% emulsion	LC_{50} – 50 h = 700 ($mg\,l^{-1}$)	(119)
Carassius auratus	PDMS (50 cs) 30% emulsion	LC_{50} – 24 h = 3,500 ($mg\,l^{-1}$)	(119)

Ecotoxicity in terrestrial compartment[119]

Species	Materials	Result or hazard rating
Plant: Soybean	Soil containing a sewage sludge with ^{14}C-PDMS was examined as nutrients for plants from germination of the seed growth to grains during a 7 month period	No significant difference from controls were observed
Insects activity: *Acheta domesticus*	PDMS (5–1,000 cs) direct apply 5 μl to the ventral thorax of insect	The time of loss of righting reflex increased with the viscosity of the PDMS, and the mortality at 48 h decreased 2 fold when the viscosity of PDMS increased 200 fold
Birds: *Anas platyrhynchos* and *Colinus virginatus*	PDMS (100 cs) was used for feed for 5 days in the diet (5,000 $mg\,kg^{-1}$ food) and kept 3 additional days on a standard food	No mortality and no other signs of toxicity occurred

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Acute oral toxicity

Species	PDMS viscosity (cs)	Result or hazard rating, LD_{50} (mg kg^{-1})	Reference
Rat	10	>4,990	(119)
Guinea pig	50	>47,750	(119)
Rat	100	>4,800	(119)
Rabbit/dog/cat	140	>9,800	(119)
Rat	350	>48,600	(119)
Rat	1,000	>4,800	(119)
Rat	350 (Baysilone M350)	>5,000	(121)
Female rat	All viscosities (SWS101 fluids)	>34,600	(122)

Acute dermal toxicity

Species	PDMS viscosity (cs)	Result or hazard rating, LD_{50} (mg kg^{-1})	Reference
Rabbit (male New Zealand)	350	No adverse effect at 24 h, LD_{50} is >19,400 mg kg^{-1} bw	(119)
Rats	50, 500, and 1,000	LD_{50} is >2,000 mg kg^{-1} bw	(119)
Rabbits	0.65–1,000,000	LD_{50} is >10,200 mg kg^{-1}	(122)

Inhalation toxicity[119]

Species	PDMS materials	Result and hazard rating, LC_{50} (mg kg^{-1})
Wistar rat	PDMS (10,000 cs) aerosol in a 25% solution in white spirit	No observed adverse effect, LC_{50}: 4 h is >11,582 mg m^{-3}
Wistar rat	Aerosol of 10,000 cs PDMS fluid 25% solution in dichloromethane	No observed adverse effect, LC_{50}: 4 h is >695 mg m^{-3}

Skin irritation[119]

PDMS viscosity (cs)	Species	Volume (ml)	Type of application	No. of applications	Duration (days)	Effects
50	Rabbit	–	Semi occlusive (continuous application to intact skin)	10	14	Nonirritating
100	Rabbit	0.5	Applied to the ears under an occlusive dressing	1	1	Nonirritating
100	Guinea pig	0.5	Draize method, 10 times per day	10 (daily)	15	Nonirritating
–	Rabbit (female, New Zealand)	0.5	Draize method	1	3	Nonirritating
1,000	Rabbit	0.5	Draize method, OEDC Guideline 404	1	7	Nonirritating

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Silicone PDMS rubber preparation[109, 123, 124]

Method	Fabricating system	Chemistry	Major applications
Room temperature vulcanizing silicone	One-part or two-part	Hydrosilylation or condensation	Sealant, adhesive, encapsulation and mold making
High temperature vulcanizing silicone	One-part or two-part from 150–230°C	Hydrosilylation or peroxide catalyzed reaction	Molded, extruded, calendered or fabric coated rubber parts (e.g., insulators, gaskets, seals, keypads, baby-bottle nipples)
Others	One-part	Electron, gamma, and UV radiation	Protective coating and cable wire insulation

Properties of PDMS elastomer

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Poisson's ratio	–	Dimethylsiloxane block in copolymer of poly[dimethylsiloxane-*b*-styrene]	0.5	(69)
Shear modulus	Pa	Unfilled PDMS elastomer ($M_n = 10{,}000$)	2.03×10^5	(125)
		Trifunctional PDMS networks	2.32×10^5	(126)
Resilience (Bashore)	%	ASTM 2632, reinforced PDMS rubber	30–65	(127)
Abrasion resistance	rev/0.254 cm	ASTM D 1630-61, reinforced PDMS rubber	155–1,600	(128)
Tear propagation	cycles/1.27 cm	ASTM D 813-59, reinforced PDMS rubber	120–150,000	(128)
Volumetric thermal expansion coefficient	K^{-1}	Reinforced PDMS rubber	$(5.9\text{–}7.9) \times 10^{-4}$	(127)
Specific heat	$kJ\,kg^{-1}\,K^{-1}$	Reinforced PDMS rubber	1.17–1.46	(127)
Hardness	Points	ASTM 2240, reinforced PDMS rubber (shore A)	30–80	(127)
Compression set	%	ASTM D 395B, reinforced PDMS rubber with post cured at 4 h/200°C		(127)
		After 22 h/177°C	~10	
		After 22 h/23°C	~10	
		After 22 h/–40°C	~30	
		After 22 h/–50°C	~100	
		After 3 years/23°C	~20	

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Properties of PDMS elastomers*[129, 130]

PROPERTY	UNITS	CONDITIONS	VALUES†			
			A	B	C	D
Specific gravity	—	ASTM D 792	1.13	1.04	1.51	1.04
Viscosity	Pa s	ASTM 4287, 10 s^{-1}	290	Nonflow	Nonflow	Nonflow
Extrusion rate	g min^{-1}	At 90 psi, 1/8 in orifice	100	350	110	440
Durometer (shore A)	points	ASTM D 2240	40	25	37	35
Tensile strength	MPa	ASTM D 412	9.0	2.24	1.55	1.79
Elongation	%	ASTM D 412	725	550	640	430
Tear strength, Die B	kN m^{-1}	ASTM D 624	37.7	4.9	6.48	5.6
Dielectric strength	kV mm^{-1}	ASTM D 149	18.5	21.7	17.4	13.5
Dielectric constant ε	—	ASTM D 150, at 100 Hz	2.98	2.8	3.69	2.77
Volume resistivity	ohm cm	ASTM D 257	3.8×10^{14}	1.5×10^{15}	6.1×10^{14}	2.4×10^{14}
Dissipation factor	—	ASTM D 150, at 100 Hz	0.0033	0.0015	0.0022	0.0035

*Prepared by vulcanization of PDMS polymer with cross-linker and reinforcement filler.
†A = Injection molded liquid silicone rubber, Silastic® LSR 9280-40. B = One-part RTV acetoxy cure, Dow Corning® 732. C = One-part RTV alcohol cure, Dow Corning® 737. D = One-part RTV oxime cure, Dow Corning® 739.

Properties of methylsiloxane resins, $(CH_3)_x(SiO)_y$*[131]

C/Si RATIO	DENSITY (g cm^{-3})	REFRACTIVE INDEX n_D^{25}
1.17	1.20	1.425
1.34	1.15	1.422
1.41	1.08	1.421
1.5	1.06	1.418

*Prepared by hydrolysis of mixed methyltrichlorosilane and dimethyldichlorosilane.

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Major producers[132]

USA	Europe	Asia
Dow Corning Corp.	Wacker Silicones Co.	Shin-Etsu Chemical Co.
General Electric Co.	Dow Corning Corp.	Dow Corning Toray Silicone Co.
Wacker Silicones Co.	General Electric Co.	GE-Toshiba Silicone Co.
McGhan NuSil Co.	Bayer AG	
OSi Specialties Inc.	Rhone-Poulenc Inc.	
	Hüls Aktiengesellschaft Th. Goldschmidt AG	

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Poly(dimethylsiloxanes), cyclic

STEPHEN J. CLARSON

ACRONYM Cyclic PDMS

CLASS Cyclic polymers

STRUCTURE $-[(CH_3)_2SiO]_x-$

INTRODUCTION Polymer molecules may have a variety of architectural structures such as linear, ring, star, branched, and ladder chains as well as three-dimensional network structures. The first synthetic cyclic polymers to be prepared and characterized were the poly(dimethylsiloxanes) (PDMS), which were reported in 1977.[1] Since that time a number of other cyclic polymers have been synthesized including cyclic polystyrene, cyclic poly(phenylmethylsiloxane), cyclic poly(2-vinylpyridine), cyclic polybutadiene, and cyclic poly(vinylmethylsiloxane).[2]

PREPARATIVE TECHNIQUES The preparation of cyclic poly(dimethylsiloxanes) is achieved by isolating the distribution of cyclic PDMS from PDMS ring-chain equilibration reactions carried out either in the bulk state or in solution. The successful utilization of such reactions for preparing large ring molecules is largely because of extensive experiments performed to characterize this system. There is also a good theoretical understanding of the reactions through the Jacobson-Stockmayer cyclization theory when used in conjunction with the rotational isomeric state model for PDMS. After attaining an equilibrium distribution of rings, vacuum fractional distillation and preparative gel permeation chromatography (GPC) may be used to prepare sharp fractions of the cyclic siloxanes having narrow molar mass distributions. Such methods allow the preparation of cyclic PDMS samples containing up to 1,000 skeletal bonds, on average, on a gram scale. The molar mass for each polymer and the polydispersity may then be characterized using techniques such as gas chromatography (GC), high-performance liquid chromatography (HPLC), analytical gel permeation chromatography (GPC), and other methods.

MAJOR APPLICATIONS Ring-opening polymerization of small rings to give linear PDMS high polymers. Copolymerization with other siloxane small rings to give copolymers of controlled composition. Both the homopolymer and copolymers are widely used as silicone fluids, elastomers, and resins.

PROPERTIES OF SPECIAL INTEREST Some selected properties of cyclic poly(dimethylsiloxanes) are given in the table below including their solution, bulk, and surface properties. It is also highlighted where significant differences are seen when compared to their linear polymeric PDMS analogs. Detailed calculations molar cyclization constants for ring-chain equilibration reactions and their dependence on the conformations of poly(dimethylsiloxane) chains and on their distributions have been described by Flory and Semlyen;[3] this approach also enables a number of properties of the rings to be theoretically calculated. The area of topological entrapment of ring polymers into network structures has also be described in the literature,[4,5] which is an area that is not accessible to linear polymers unless they undergo end-cyclizing chemistry. This concept of topological threading is somewhat general for ring molecules as it may also be utilized in the preparation of novel catenanes and rotaxanes.

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Selected properties of the cyclic poly(dimethylsiloxanes) (r) compared to linear poly(dimethylsiloxanes) (l)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Characteristic ratio $\langle r^2 \rangle / nl^2$	–	Derived from molar cyclization equilibrium constants in the bulk state at 383 K	6.8	(6)
Density	$kg\,m^{-3}$	At 298 K ($x = 95$)	971.67	(7)
Glass transition temperature $T_g(\infty)$	K	–	149.8	(4, 8)
Melting point	K	$M_n = 24{,}370\,g\,mol^{-1}$		(8)
		T_{m1}	227.0	
		T_{m2}	237.8	
Raman absorption ν_s(Si–O)	cm^{-1}	Crystalline region	466	(9)
		Amorphous region	486	
Activation energy	kJ	For viscous flow $E_{visc}(\infty)$	15.5	(10, 11)
Static dielectric permittivity ε_o	–	At 298 K ($x = 95$)	2.757	(7)
Root mean square dipole moment	C m	$10^{30}\ \langle \mu^2 \rangle^{1/2}$ at 298 K ($x = 95$)	14.3	(7)
Refractive index	–	At 298 K ($x = 95$)		(7)
		632.8 nm	1.4025	
		436.0 nm	1.4140	
Onset temperature for thermal depolymerization	K	Under N_2	623	(12)
Intrinsic viscosities $[\eta]_r/[\eta]_l$	–	In butanone (θ-solvent) at 293 K	0.67	(1, 13)
		In cyclohexane at 298 K	0.58	
		In bromocyclohexane (θ-solvent) at 301 K	0.66	
Diffusion coefficients D_r/D_l	–	In PDMS networks at 296 K	1.18 ± 0.03	(11, 14, 15)
		In toluene at 298 K	0.84 ± 0.01	
Means square radius of gyration $\langle s^2 \rangle_{z,l}/\langle s^2 \rangle_{z,r}$	–	In benzene d_6 at 292 K	1.90	(11)
Translational friction coefficients f_r/f_l	–	In toluene at 298 K	0.83 ± 0.01	(10, 11, 14)
Number-average molar masses of PDMS rings and chains	–	With the same GPC retention values M_r/M_l	1.24 ± 0.04	(10, 11)
Melt viscosities	–	At η_r/η_l for $M_w = 24{,}000\,g\,mol^{-1}$	0.45 ± 0.02	(11)

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Poly(dimethylsilylene)

ROBERT WEST

ACRONYM, ALTERNATIVE NAME PDMS, polydimethylsilane

CLASS Polysilanes

STRUCTURE $-(Me_2Si)_n-$

MAJOR APPLICATIONS Precursor to silicon carbide ceramics via intermediate pyrolysis to polycarbosilane.[1]

PROPERTIES OF SPECIAL INTEREST Relatively low cost, compared with other polysilanes.
For general information about polysilane polymers see the entry for *Poly(methylphenylsilylene)* in this handbook.

Preparative techniques[2,3]

Reactants	Solvent	Temp. (°C)	Yield (%)
Me_2SiCl_2, Na	Toluene	110	80
	Octane	125	–

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Typical comonomers for copolymerization			$PhMeSiCl_2$, Ph_2SiCl_2	
Repeat unit	$g\,mol^{-1}$	$(CH_3)_2Si$	58	–
IR absorption	cm^{-1}	–	2,950, 2,890, 1,905, 1,250, 835, 750, 695, 632	(2)
UV absorption	λ (nm)	Solid	340	(3)
NMR spectra	δ (ppm)	Solid; ^{29}Si nucleus	−34.45	(3)
Solvents	Fluorene (220°C), α-chloronaphthalene (238°C)			
Nonsolvents	Toluene, THF, hexane, 2-propanol, CH_2Cl_2, acetone			
Lattice	–	–	Monoclinic	(3)
Monomers per unit cell	–	–	2	(3)
Unit cell dimensions	Å	–	$a = 12.18$, $b = 8.00$, $c = 3.88$	(3)
Unit cell angles	Degrees	–	$\alpha = \beta = \gamma = 90$	(3)
Transition temperature	K	$2.5\,cal\,g^{-1}$ $0.3–0.8\,cal\,g^{-1}$	333 499	(3)

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Poly(dimethylsilylene)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	–	0.971	(2)
Electronic conductivity	$S\,cm^{-1}$	Undoped H_2SO_4	$<10^{-12}$ 10^{-3}	(4)
Suppliers	Nippon Soda Co. Ltd., 2-1, Ohtemachi 2-chome, Chiyoda-ku, Tokyo 100, Japan Gelest Inc., 612 William Leigh Drive, Tullytown, PA 19007-6308, USA			

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Poly(dimethylsilylene-*co*-phenylmethylsilylene)

ROBERT WEST

ACRONYM, ALTERNATIVE NAME PSS, polysilastyrene

CLASS Polysilanes

STRUCTURE $[-(Me_2Si)_n(PhMeSi)_m-]$ (n, $m = 0.5$–2)

MAJOR APPLICATIONS Precursor for silicon carbide ceramic.[1,2] Initiator for free-radical polymerization.[3]

PROPERTIES OF SPECIAL INTEREST None. For general information about polysilane polymers see the entry for *Poly(methylphenylsilylene)* in this handbook.

GENERAL INFORMATION Polysilastyrene is a copolymer of Me_2Si units ($58\,g\,mol^{-1}$) with PhMeSi units ($120\,g\,mol^{-1}$). As ordinarily prepared by cocondensation of Me_2SiCl_2 and $PhMeSiCl_2$, it is somewhat blocklike, but a more ordered polymer is obtained from $ClSiMe_2SiMePhCl$. The polymer is atactic and amorphous. The molecular weight distribution is bi- or polymodal.

Preparative techniques

Reactants	Solvent	Temp. (°C)	Yield (%)	M_w	Reference
$PhMeSiCl_2$, Me_2SiCl_2, Na	Toluene	110	49	40,000 39,000 14,000	(4)
$ClSiMePhSiMe_2Cl$, Na	Toluene	110	45	600,000 4,000	(5)

PROPERTY	UNITS	CONDITION		VALUE	REFERENCE
UV absorption	λ (nm)	THF, ε/repeat = 8,000		330	(4)
		THF, ε/repeat = 6,000		320	(5)
NMR spectra	δ (ppm)	Nucleus	Conditions		
		^{29}Si	Random polymer, C_6D_6 solution	−36.6 −37.4 −38.2 to −40.4	(5)
		^{29}Si	Ordered polymer	−35 to −39	(5)
		^{29}Si	Solid	−45	(6)

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Poly(dimethylsilylene-*co*-phenylmethylsilylene)

PROPERTY	UNITS	CONDITION		VALUE	REFERENCE
NMR spectra	δ (ppm)	Nucleus	Conditions		
		^{13}C	Random polymer, C_6D_6 solution	127.4 134.7 137.0 −3.8 −5.3 −6.2 −6.9	(4)
Solvents	THF, toluene, CH_2Cl_2				
Nonsolvents	Hexane, 2-propanol				
Electronic conductivity	$S\,cm^{-1}$	Undoped polymer AsF_5, 15 Torr SbF_5, 5 Torr		$<10^{-12}$ 1.5×10^{-6} 5×10^{-7}	(1)
Suppliers	Nippon Soda Co. Ltd., 2-1, Ohtemachi 2-chome, Chiyoda-ku, Tokyo 100, Japan Gelest Inc., 612 William Leigh Drive, Tullytown, PA 19007-6308, USA				

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Poly(1,3-dioxepane)

EVARISTO RIANDE AND JULIO GUZMÁN

ACRONYM PDXP

CLASS Polyformals

STRUCTURE $[-CH_2-O-CH_2-CH_2-CH_2-CH_2-O-]$

MAJOR APPLICATIONS None known

PROPERTIES OF SPECIAL INTEREST None known

PREPARATIVE TECHNIQUES Cationic polymerization of 1,3-dioxepane in solution or in bulk at temperatures normally lower than 25°C. Initiators: Lewis acids, oxonium salts, etc.[1–4]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Ceiling temperature	K	Initiator: ClO_4H in CH_2Cl_2 Initiator: BF_3 in bulk	300 517	(5) (6)
Typical comonomers	Isobutyl vinyl ether, 1,3-dioxolane			(7, 8, 9)
Specific volume	$cm^3\ g^{-1}$	Amorphous Crystal	$0.94 + (3.1 \times 10^{-4})T$ $0.813 + (2.4 \times 10^{-4})T$	(10)
Solvents	Almost all the organic solvents			
Nonsolvents	Alkanes			
Solubility parameter	$(MPa)^{1/2}$	From viscosity measurements	18.81	(3)
Cohesive energy density	MPa	From viscosity measurements	353.6	(3)
Lattice	–	–	Orthorhombic	(11)
Space group	–	–	P2cn (C_{2v})	(11)
Monomers per unit cell	–	–	2	(11)
Unit cell dimensions	Å	Chain axis	$a = 8.50$ $b = 4.79$ $c = 13.50$	(11)
Degree of crystallinity	%	$M_n = 1.2 \times 105$	35	(10)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of fusion	$kJ\,mol^{-1}$	DSC	14.454	(10)
			14.3	(12)
Entropy of fusion	$kJ\,K^{-1}\,mol^{-1}$	DSC	0.0477	(10)
Avrami exponent	–	Dilatometry	3	(10)
Glass transition temperature T_g	K	DSC		
		$M_n = 1 \times 10^5$	192	(2)
		$M_n = 3,500$	179	(2)
		–	189	(12)
Equilibrium melting temperature $T_m{}^{\circ}$	K	Dilatometric data. Extrapolation T_m vs. T_c	303	(10)
Melting temperature T_m	K	DSC	296	(12)
			297	(11)
Heat capacity	$KJ\,K^{-1}\,mol^{-1}$	Crystal ($T_g < T < T_m$)	$(0.189 \times 10^{-3}) + (4.2 \times 10^{-6})T$	(12)
		Amorphous ($T > T_m$)	$(1.38 \times 10^{-3}) + (1.76 \times 10^{-6})T$	
Dipolar ratio $\langle\mu^2\rangle_0/nm^2$	–	30°C	0.158	(4)
$d\ln\langle\mu^2\rangle_0/dT$	K^{-1}	–	5.4×10^{-3}	(4)
Molecular conformation	$-CH_2-CH_2-CH_2-CH_2-O-CH_2-O-CH_2-CH_2-CH_2-CH_2-O-CH_2-O-$ T T T G T G G T T T G T G G			(4, 11)

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Poly(1,3-dioxolane)

EVARISTO RIANDE AND JULIO GUZMÁN

ACRONYM PDXL

CLASS Polyacetals

STRUCTURE $[-CH_2-O-CH_2-CH_2-O-]$

MAJOR APPLICATIONS None known. Stabilizer of Delrin by copolymerization with trioxane.

PROPERTIES OF SPECIAL INTEREST Possible use as a modifier for elastomers.

PREPARATIVE TECHNIQUES Cationic polymerization of 1,3-dioxolane in solution or in bulk at temperatures normally lower than 25°C. Initiators: Lewis acids, oxonium salts, etc.[1]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Ceiling temperature	K	Initiators		
		$HClO_4$ in CH_2Cl_2	274	(2)
		BF_3OEt_2 in benzene	265	(3)
		BF_3 in $CDCl_3$	320	(4)
		$HClO_4$ in bulk	417	(5)
Typical comonomers	Cyclic ethers, cyclic acetals,diketene, lactones, styrene			(6, 7–10, 11, 12, 13)
Specific volume	$cm^3\ g^{-1}$	Amorphous	$0.796 + (7.64 \times 10^{-4})T$	(14)
		Crystal II	$0.6965 + (5.0 \times 10^{-4})T$	
		Crystal III	$0.7350 + (6.5 \times 10^{-4})T$	
Thermal expansion coefficient	K^{-1}	Liquid (dilatometry)	6.73×10^{-4}	(15)
		Glass (thermal mechanical analysis)	3.40×10^{-4}	
Solvents	Chlorinated solvents (methylene chloride, chloroform, etc.), aromatic (benzene, toluene, etc.), ketones, ethers			
Nonsolvents	Hydrocarbons (pentane, hexane)			
Solubility parameter	$(MPa)^{1/2}$	From viscosity measurements	20.67	(16)
Virial coefficient	$cm^3\ mol^{-1}\ g^{-2}$	In tetrahydrofuran at 25°C		(17)
		$M_n = 1.1 \times 10^5$	9.15×10^{-4}	
		$M_n = 9 \times 10^4$	9.40×10^{-4}	
		$M_n = 6.6 \times 10^4$	9.48×10^{-4}	
		$M_n = 3.55 \times 10^4$	9.78×10^{-4}	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Characteristic ratio $C_\infty = \langle r^2 \rangle_0 / nl_2$	–	From virial coefficient	3.7	(17)
Temperature coefficient of unperturbed dimensions $d \ln\langle r^2 \rangle_0 / dT$	K^{-1}	Intrinsic viscosities	0.2×10^{-3}	(18)
Cohesive energy density	MPa	From viscosity measurements	427	(16)
Degree of crystallinity	%	$M_w = 1.2 \times 10^5$ $M_w = 8.8 \times 10^3$	55 80	(19)
Heat of fusion	$kJ\,mol^{-1}$	DSC	16.698 ± 0.32 15.49	(20) (21)
Entropy of fusion	$kJ\,K^{-1}\,mol^{-1}$	DSC	0.0423	(21)
Avrami exponent	–	DSC, crystallization between 0 and 21°C Dilatometry	2 3	(22) (19)

Unit cell dimensions[23, 24]

Lattice and space group	Monomers per unit cell	Cell dimensions (Å)			Cell angles		
		a	*b*	*c* (Chain axis)	α	β	γ
Triclinic	15	12.32	4.66	24.7	–	–	–
Orthorhombic, Pbca-D_{2H}^{15}	8	9.07	7.79	9.85	–	–	–
Hexagonal	18	8.07	8.07	29.5	–	–	120

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature T_g	K	DSC	209 210	(20) (15)
Equilibrium melting temperature T_m	K	Dilatometric data. Extrapolation T_m vs. T_c Low molecular weight High molecular weight	 352 358, 366	 (22) (19, 22)
Melting temperature T°_m	K	DSC	333 325	(25) (20)
Heat capacity	$KJ\,K^{-1}\,mol^{-1}$	Crystal ($T_g < T < T_m$) Amorphous ($T > T_m$)	$(0.189 \times 10^{-3}) + (3.7 \times 10^{-6})T$ $(1.396 \times 10^{-3}) + (1.472 \times 10^{-6})T$	(20)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dipolar moment ratio $\langle \mu^2 \rangle_0 / nm^2$	—	30°C	0.17	(26)
$d \ln \langle \mu^2 \rangle_0 / dT$	K^{-1}	30–60°C	6.0×10^{-3}	(26)
Intrinsic viscosity $[\eta]$	$dl\,g^{-1}$	Chlorobenzene in tetrahydrofuran at 25°C ($3.55 \times 10^4 < M_n < 1.1 \times 10^5$)	$[0] = 0.002\,M^{0.5}$ $[0] = 1.7 \times 10^{-4}\,M_n^{0.73}$	(27) (17)
Molecular conformation	O—CH$_2$—O—CH$_2$—CH$_2$— G′ G′ T′ G′ G′ 79 74 173 −63 −94			(23)

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Poly(di-*n*-pentylsiloxane)

YULI K. GODOVSKY AND VLADIMIR S. PAPKOV

ACRONYM PDPeS

CLASS Polysiloxanes

STRUCTURE $[-(C_5H_{11})_2SiO-]$

PROPERTIES OF SPECIAL INTEREST Low glass transition temperature, mesophase behavior.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Preparative technique	Anionic ring-opening polymerization of hexapentylcyclotrisiloxane			(1, 2)
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	186.36	–
Typical molecular weight range of polymer	$g\,mol^{-1}$	–	10^4–10^6	–
NMR spectroscopy	Solid state ^{29}Si			(2, 3)
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ $a =$ None	Toluene, 298 K	$K = 0.741$ $a = 0.514$	(3)
Heat of fusion	$kJ\,mol^{-1}$	High temperature crystal 2 to mesophase	1.9	(3–5)
Entropy of fusion	$J\,mol^{-1}\,K^{-1}$	–	7.6	(3–5)
Glass transition temperature	K	DSC	167	(3)
Melting temperature	K	High temperature crystal 2 to mesophase	250	(3–5)
Polymorphs	Low temperature crystal 1; DSC, X-ray data High temperature crystal 2 Mesophase			(3–5) (3–5) (3–5)
Transition temperature	K	Crystal 1–crystal 2, DSC	235	(3–5)
Heat of transition	$kJ\,mol^{-1}$	Crystal 1–crystal 2	9.0	(3)
Isotropization temperature	K	Polarization microscopy	603	(3)

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Poly(diphenylsiloxane)

DALE J. MEIER

ACRONYM PDPS

CLASS Polysiloxanes

STRUCTURE $[-Si(C_6H_5)_2O-]$

MAJOR APPLICATIONS PDPS is not a commercial polymer. Diphenylsiloxane is a component in various copolymers.

PROPERTIES OF SPECIAL INTEREST Highly crystalline, high melting point, excellent thermal stability, mesomophic state at high temperatures.

PREPARATIVE TECHNIQUES	CONDITIONS	REFERENCE
Anionic	From hexaphenylcyclotrisiloxane	
	Li alkyl, bulk	(1)
	KOH, bulk	(2, 3)
	Li alkyl, solution	(4, 5)
Condensation	From diphensilanediol	(6)
Typical comonomer	Dimethylsiloxane	
	Random	(4, 7–9)
	Block	(1, 4, 5, 10)

Crystalline state properties

Lattice	Cell dimensions (Å) *a*	*b*	*c*	Cell angles (degrees) α	β	γ	Reference
Pbn21, hexagonal pacxking in quasi-planar sequential configuration	20.145	9.820	4.944	90	90	90	(11)
Rhombic unit cell, 2 monomers per cell	20.1	10.51	10.24	—	—	—	(18)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Solvents	K	Diphenyl ether	>410	—
		1-Chloronaphalene	>410	—
		1,2,4 Trichlorobenzene	>410	—
		From quenched state: chloroform, toluene	320	(4)
Density	$g\,cm^{-3}$	Experimental	1.22	(13)
		Unit cell	1.26–1.3	(11)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melting temperature	K	To mesomorphic state	538	(16)
			545	(14)
			503	(15)
		Oligomers	471, 481, 487	(19)
Transition temperature	K	To isotropic state	813	(16)
Heat of fusion	$J\,g^{-1}$	To mesomorphic state	35.5	(14)
			20.4	(15)
Entropy of fusion	$J\,K^{-1}\,mol^{-1}$	–	12.8	(14)
			7.98	(15)
Glass transition temperature	K	DSC	313	(16)
			322	(3)
Thermal stability	K	TGA, 10% weight loss, $10^{\circ}\,min^{-1}$ under N_2	784	(16)
Dielectric constant	–	MW = 1,500–2,600	3.5–2.2	(17)
Dielectric loss	–	MW = 1,500–2,600	0.004–0.5	(17)
Elastomer reinforcement	–	In dimethylsiloxane elastomers	–	(6)
Sequence distributions and crystallinity in copolymers with dimethylsiloxane	–	Computer simulations	–	(20, 21)
Light emission (peak emmision)	nm	KrF laser irradiation, 248 nm	340	(22)

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Poly(di-*n*-propylsiloxane)

YULI K. GODOVSKY AND VLADIMIR S. PAPKOV

ACRONYM PDPrS

CLASS Polysiloxanes

STRUCTURE $[-(C_3H_7)_2SiO-]$

PROPERTIES OF SPECIAL INTEREST Low glass transition temperature, mesophase behavior.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Preparative technique	Anionic ring-opening polymerization of hexapropylcyclotrisiloxane			(1–4)
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	130.26	–
Typical molecular weight range of polymer	$g\,mol^{-1}$	–	10^3–10^5	–
NMR spectroscopy	–	Solid state ^1H, ^{29}Si		(3, 5)
Theta temperature	K	Toluene 2-Pentanone	283 351	(6)
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None	Toluene, 25°C, MW = $(2.5–30) \times 10^5$ Toluene, 10°C 2-Pentanone, 78°C	$K = 4.35 \times 10^{-2}$, $a = 0.58$ $K = 1.09 \times 10^{-1}$, $a = 0.5$ $K = 8.71 \times 10^{-2}$, $a = 0.5$	(6)
Characteristic ratio $\langle r^2 \rangle / nl^2$	–	–	13.0 ± 1.0	(6–8)

Unit cell dimensions[9]

Polymorph	Lattice	Monomers per unit cell	Cell dimension (Å)			Cell angles (degrees)		
			a	*b*	*c* (chain axis)	α	β	γ
High temperature β_2	Tetragonal Space group $P4_1$ or $P4_3$	4 Helix 4_1	9.52	9.52	9.40	90	90	90

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Poly(di-*n*-propylsiloxane)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of fusion	$kJ\,mol^{-1}$	$\beta_2 \rightarrow \mu$ (mesophase)	2.86	(2, 10, 11)
Heat of isotropization	$kJ\,mol^{-1}$	$\mu \rightarrow$ isotropic melt	0.42	(2, 10, 11)
Entropy of fusion	$J\,mol^{-1}\,K^{-1}$	$\beta_2 \rightarrow \mu$	8.59	(2, 10, 11)
Entropy of isotropization	$J\,mol^{-1}\,K^{-1}$	$\mu \rightarrow$ isotropic melt	0.88	(2, 10, 11)
Density (crystalline)	$g\,cm^{-3}$	From X-ray data, β_2, 293 K	1.015	(9)
Glass transition temperature	K	DSC	164	(2, 3, 10, 11)
Melting temperature	K	$\beta_2 \rightarrow \mu$	333	(2, 10, 11)
Polymorphs	Low temperature β_1 (tetragonal)			(2, 10–13)
	High temperature β_2 (tetragonal)			(2, 9–13)
	Low temperature α_1 (monoclinic ?)			(12–13)
	High temperature α_2 (monoclinic ?)			(12–14)
Transition temperature	K	$\beta_1 \rightarrow \beta_2$	218	(2, 10, 11)
Heat of transition	$kJ\,mol^{-1}$	$\beta_1 \rightarrow \beta_2$	2.04	(2, 10, 11)
Isotropization temperature	K	MW ($\times 10^3$) =		(16, 17)
		87	480	
		68	450	
		51	445	
		43	418	
		≈ 10	No mesophase	

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Poly(epichlorohydrin)

QINGWEN WENDY YUAN

ACRONYM PECH

CLASS Polyethers

STRUCTURE $[-CH_2-CH(CH_2Cl)-O-]$

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (repeat unit)	$g\,mol^{-1}$	–	92.5	–
Polymerization	–	–	Ring-opening	(1, 2)
Typical copolymers	Epichlorohydrin (EPI)-ethylene oxide (EO) copolymer EPI-allyl glycidyl ether (AGE) copolymer EPI-EO-AGE terpolymer			(3)
Glass transition temperature	K	$n = 5{,}000$–$20{,}000$ Heating rate $= 20\,K\,min^{-1}$	258.5 251	(2) (3, 4)
Tensile strength	MPa	–	17	(5)
Elongation	%	–	280	(5)
Engineering modulus	MPa	Elongation = 100% Elongation = 200%	5.1 12.6	(5)
Hardness	Shore A	–	72	(5)
Tear strength	$kN\,m^{-1}$	–	36	(5)
Compression set	%	70 h at 100°C 70 h at 150°C	26 57	(5)
Volume change	%	70 h, ASTM Fuel A, 20°C 70 h, ASTM Fuel C, 20°C 70 h, ASTM Oil #1, 150°C 70 h, ASTM Oil #3, 150°C	0 25 0 1	(5)
Surface tension	$mN\,m^{-1}$	$M = 1{,}500$, $T = 293.5\,K$	43.2	(3)
Fractionation	–	Extraction; precipitation	Acetone (cold), acetone/methanol, methanol/water	(3)

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Poly(epichlorohydrin)

Crystalline-state properties[3]

Lattice	Space group	Unit cell parameters (Å)			Monomers per unit	Density ($g\,cm^{-3}$)
		A	*B*	*C*		
Orthorhombic	D2-4 or C2V-9	12.14	4.90	7.07	4	1.461
Orthorhombic	C2V-9	12.16	4.90	7.03	4	1.467
Orthorhombic	—	12.24	4.92	6.96	4	1.466
Orthorhombic	D2-4	12.15	4.86	7.07	4	1.472

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Poly(erucic acid dimer anhydride)

ABRAHAM J. DOMB AND ROBERT LANGER

ACRONYMS, TRADE NAMES BIODEL-EAD, Poly(EAD), Poly(EAD-SA)

CLASS Polyanhydrides

STRUCTURE

$$\begin{array}{l} -\!\!\!\!\left[CO-(CH_2)_7-\underset{|}{C}H-(CH_2)_8-CH_3 \right. \\ \left. \quad CH_3-(CH_2)_8-CH-(CH_2)_7-COO \right]\!\!\!\!- \end{array}$$

MAJOR APPLICATIONS Biodegradable polymer for controlled drug delivery in a form of implant, film, or injectable microspheres (e.g., Septacin^{TM}–gentamicin-loaded linked beads for the treatment of chronic bone infections).

PROPERTIES OF SPECIAL INTEREST Anhydride copolymers of erucic acid dimer (EAD) with aliphatic diacids such as sebacic acid (SA) degrade in a physiological medium to EAD and SA. Matrices of the copolymers loaded with dissolved or dispersed drugs degrade in vitro and in vivo to constantly release the drugs for periods from 1–12 weeks.

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Molecular weight		P(EAD-SA)			(1)
	10^4 g mol^{-1}	GPC-polystyrene standards	$M_w = 3$–30, $M_n = 1$–3		
	dL g^{-1}	Viscosity 25°C, dichloromethane	$\eta_{sp} = 0.2$–1.4		
IR (characteristic absorption frequencies)	cm^{-1}	PSA, P(EAD-SA), or P(EAD) film on NaCl pellet	1,740, 1,810		(1)
UV (characteristic absorption wavelength)	nm	P(EAD-SA), EAD monomer dichloromethane	253		–
Optical rotation	–	Dichloromethane	No optical rotation		–
Solubility	mg ml^{-1}	25°C	P(EAD)	P(EAD-SA)	(2)
		Chloroform	>300	<300	
		Dichloromethane	>300	<300	
		Tetrahydrofuran	180	100	
		Ketones	80	50	
		Ethyl acetate	30	25	
		Ethers	5	3	
		Alkanes and arenes	<1	<1	
		Water	<1	<1	
Mark–Houwink parameters: K and a	K = ml g^{-1} a = None	$CHCl_3$, 23°C	$K = 3.46$ $a = 0.634$		(1)

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Poly(erucic acid dimer anhydride)

PROPERTY	UNITS	CONDITIONS	VALUE				REFERENCE
Thermal properties	mol %	P(EAD-SA), DSC, 10°C min^{-1}	0:100	8:92	22:78	100:0	(2)
	K	T_m	359.0	348.0	337.0	293.0	
	K	T_g	333.1	<283.0	<283.0	<273.0	
	kJ kg^{-1}	ΔH	150.7	50.2	13.0	4.0	
Crystallinity	%	–	66	54	35	<5	
Stability in chloroform (decrease in M_w) (anhydride interchange depolymerization)			P(EAD-SA)				
			0:100		22:78		
Depolymerization rate constant	t^{-1}	37°C	0.1325		0.1233		
Tensile strength	MPa	Film by melt, P(EAD-SA) 22:78, $M_w = 1.55 \times 10^5$ g mol^{-1}	4.2				(1)
Tensile modulus	MPa	Film by melt, P(EAD-SA) 22:78, $M_w = 1.55 \times 10^5$ g mol^{-1}	45				(1)
Elongation yield	%	Film by melt, P(EAD-SA) 22:78, $M_w = 1.55 \times 10^5$ g mol^{-1}	14				(1)
Elongation at break	%	Film by melt, P(EAD-SA) 22:78, $M_w = 1.55 \times 10^5$ g mol^{-1}	85				(1)
Erosion rate, SA release	mg h^{-1}	14 × 2.7 mm P(EAD-SA) disc, 0.1 M phosphate buffer, pH 7.4, 37°C	0.3				(2)
Erosion front	mm day^{-1}	–	188				
Elimination time in vivo	days	Implant in dog bone	35				(3)
Drug release in vitro	% day^{-1}	From P(EAD-SA) 22:78					(1)
		Hydrophilic drugs (i.e. gentamicin, carboplatin)	3–6				
		Hydrophobic drugs (i.e., taxol, dexamethasone)	1–3				
Drug release in vivo	% day^{-1}	Beads of 20% gentamicin in rabbit bone	5				(3)
Biocompatibility	Compatible with human bone and muscle Compatible with rabbit brain, bone, muscle, subcutane						(1)
Supplier	Guilford Pharmaceuticals, Inc., Baltimore, Maryland, USA						

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Polyesters, unsaturated

MEE Y. SHELLEY

TRADE NAMES Dion, Hetron, Polylite, Advaco, Altek, Cargill, Cook, OCF, Pedigree, Pioester, etc.

CLASS Thermoset polymers (mixtures of polyester prepolymers with aliphatic unsaturation and a vinyl monomer)

PRINCIPAL COMPONENTS Prepolymers (oligomer): glycols (e.g., 1,3-propylene glycol), saturated acids (e.g., phthalic anhydride/acid), unsaturated acids (e.g., maleic anhydride/acid). Monomers: styrene, α-methylstyrene, methyl acrylate, methyl methacrylate, etc.

OTHER INGREDIENTS Inhibitors to prevent premature cross-linking and to allow a suitable shelf life (e.g., hydroquinone). Initiators (catalysts): methyl ethyl ketone peroxides, benzoyl peroxides, etc. Accelerators: cobalt naphthenate, cobalt octanoate, etc.

MAJOR APPLICATIONS Laminates, coatings, art objects, insulation, construction (e.g., bath tubs, floor tiles, countertops, roofing, siding, skylights, fences, etc.), automobile parts, embedding of specimens (e.g., decorative, zoological), encapsulation of electronic assemblies, toys, playground equipment, furniture, pearl buttons, sports equipment (snow boards, skis, bowling balls, etc.), chemical storage tanks.

PROPERTIES OF SPECIAL INTEREST Low cost, excellent wetting and surface quality, ease of moldability, versatility, processible over a wide temperature range, high impact resistance, good weathering resistance, high cure shrinkage.

PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Linear mold shrinkage	Ratio	Unfilled	0.001–0.007	(1)
		Glass fiber-reinforced	0.0002–0.012	(2)
		SMC, glass fiber-reinforced	0.00002	(3, 4)
		BMC, glass fiber-reinforced		(3, 4)
		Compression	0.00001	
		Injection	0.00004	
		EMI shielding (conductive)	0.0002–0.001	(2)
Processing temperature	K	Glass fiber-reinforced		(2)
		Preformed, chopped roving, (compression)	350–430	
		Premix, chopped glass, (compression)	410–450	
		Woven cloth, (compression)	296–390	
		Molding, glass fiber-reinforced		
		Compression	405–470	
		Injection	405–470	
		Transfer	405–450	

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PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Processing temperature	K	EMI shielding (conductive)		(2)
		Compression	405–470	
		Injection	405–460	
		Transfer	410–430	
Molding pressure	MPa	Glass fiber-reinforced		(2)
		Preformed, chopped roving	1.7–14	
		Premix, chopped glass	3.4–14	
		Woven cloth	2.1	
		SMC, glass fiber-reinforced	2.1–14	
		SMC, BMC, glass fiber-reinforced, low-density	3.4–14	
		SMC, glass fiber-reinforced, low pressure	1.7–5.5	
		SMC, glass fiber-reinforced, low shrink	3.4–14	
		BMC, TMC, glass fiber-reinforced	2.8–7.6	
		EMI shielding (conductive)	3.4–14	
Viscosity	Pa s	Brookfield model lvf #3 spindle at 60 rpm		(5)
		Cast, rigid	0.65–0.85	
		Cast, flexible	1.1–1.4	
Specific gravity	—	Cast, rigid	1.04–1.46	(2)
		Cast, flexible	1.01–1.20	
		Glass fiber-reinforced		
		Preformed, chopped roving	1.35–2.3	
		Premix, chopped glass	1.65–2.3	
		Woven cloth	1.5–2.1	
		SMC, glass fiber-reinforced	1.65–2.6	
		SMC, glass fiber-reinforced, low density	1.0–1.5	
		BMC, TMC, glass fiber-reinforced	1.72–2.1	
		EMI shielding (conductive)	1.75–1.85	
Water absorption	%	1/8 in. thick sample, 24 h		
		Cast, rigid	0.15–0.6	(2)
		Cast, flexible	0.5–2.5	(2)
		SMC, glass fiber-reinforced	0.1–0.5	(3, 4)
		BMC, glass fiber-reinforced	0.20	(3, 4)
		Pultruded, glass fiber-reinforced	0.75	(3, 4)
		Spraying/lay-up, glass fiber-reinforced	1.30	(3, 4)
		Woven roving, lay-up, glass fiber-reinforced	0.50	(3, 4)
Volume resistivity	ohm cm	Unspecified	10^{14}	(5)
		Glass fiber-reinforced SMC, compression	5.7×10^{14}	(3, 4)
		BMC, compression	27×10^{14}	(3, 4)
		Pultruded	10^{13}	(3, 4)
		Woven roving, lay-up	10^{14}	(3, 4)
Dielectric constant	—	At 1 MHz, cast	2.8–3.0	(1)
		At 1 MHz, molding	3.2–4.5	(1)
		Glass fiber-reinforced	5	(6)

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PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Dissipation factor	—	At 1 MHz	0.02	(5)
Thermal conductivity	$W\ m^{-1} K^{-1}$	Glass fiber-reinforced		(3, 4)
		BMC, compression or injection	8.37	
		Pultruded	6.92	
		Spraying/lay-up	2.60	
Specific heat	$J\,kg^{-1} K^{-1}$	Glass fiber-reinforced		(3, 4)
		SMC or BMC	1.26	
		Pultruded	1.17	
		Spraying/lay-up	1.30	
Deflection temperature	K	Under 1.82 MPa		
		Cast, rigid	330–480	(2)
		Blend (flexible:rigid = 30:70)	324	(5)
		Blend (flexible:rigid = 20:80)	331	(5)
		Blend (flexible:rigid = 10:90)	336	(5)
		Blend (flexible:rigid = 5:95)	358	(5)
		Glass fiber-reinforced	430–560	(2)
		EMI shielding (conductive)	470 – 480+	(2)
Maximum resistance to continuous heat	K	Glass-reinforced	430	(6)
Arc resistance	s	SMC or BMC, glass fiber-reinforced	188–190	(3, 4)
		Pultruded, glass fiber-reinforced	80	
Flash point	K	Cast, rigid or flexible, Seta closed cup	305	(5)

*SMC = sheet molding compounds; BMC = bulk molding compounds; TMC = thick molding compounds; EMI = electromagnetic interference.

Resistance to chemicals[(6)]

Conditions	Satisfactory resistance to:	Questionable resistance to:
Glass-reinforced, 298 K	Nonoxidizing acids Aqueous salt solutions Polar organic solvents Water	Oxidizing acids Aqueous alkalies Nonpolar solvents

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Radiation resistance, half-value dose in air*

Conditions	Determined by:	Dose rate ($Gy\,h^{-1}$)	Value (MGy)	Reference
Filled with glass fiber	Flexural strength	$\geq 10^5$	10–50	(7, 8)
Filled with mineral flour and glass fiber	Flexural strength	$\geq 10^5$	>30	(7, 9)
Filled with mineral flour and glass fiber	Impact strength	$\geq 10^5$	>10	(7, 9)
Filled with mineral flour and glass fiber (50% mineral flour)	Flexural strength	10	>1	(7, 9)
Filled with mineral flour and glass fiber (15% glass fiber)	Impact strength	10	>0.5	(7, 9)
Filled with mineral flour (82% quartz sand)	Flexural strength	500	>7	(7, 10)

*Defined as the absorbed dose that reduces the mechanical property in the second column to 50% of the initial value.

PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Tensile strength at break	MPa	Cast, rigid	4.1–90	(2)
		Cast, flexible	3.4–21	(2)
		Glass fiber-reinforced		
		Preformed, chopped roving	100–210	(2)
		Premix, chopped glass	21–69	(2)
		Woven cloth	210–340	(2)
		Pultruded	207	(3, 4)
		SMC, glass fiber-reinforced	28–170	(2)
		BMC, TMC, glass fiber-reinforced	21–90	(2)
		EMI shielding (conductive)	28–55	(2)
Elongation at break	%	Cast, rigid	<2.6	(2, 5)
		Cast, flexible	40–310	(2)
		Blend (flexible : rigid = 30 : 70)	10	(5)
		Blend (flexible : rigid = 20 : 80)	4.8	(5)
		Blend (flexible : rigid = 10 : 90)	1.7	(5)
		Blend (flexible : rigid = 5 : 95)	1.3	(5)
		Glass fiber-reinforced	0–5	(2)
Compressive strength (rupture or yield)	MPa	Cast, rigid	90–210	(2)
		Glass fiber-reinforced		
		Preformed, chopped roving	100–210	(2)
		Premix, chopped glass	140–210	(2)
		Woven cloth	170–340	(2)
		Pultruded	207	(3, 4)
		Glass fiber-reinforced	172	(6)
		Molding, glass fiber-reinforced	97–210	(2)
		EMI shielding (conductive)	120–170	(2)

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PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Flexural strength (rupture or yield)	MPa	Cast, rigid	60–160	(2)
		Glass fiber-reinforced		
		Preformed, chopped roving	70–280	
		Premix, chopped glass	50–140	
		Woven cloth	280–550	
		Molding, glass fiber-reinforced	62–250	
		EMI shielding (conductive), SMC, TMC	120–140	
		EMI shielding (conductive), BMC	83	
Tensile modulus	MPa	Cast, rigid	2,100–4,400	(2)
		Glass fiber-reinforced	5,500–31,000	
Flexural modulus	MPa	Cast, rigid, 296 K	3,400–4,200	(2)
		Glass fiber-reinforced		
		Preformed, chopped roving, 296 K	7,000–21,000	(2)
		Premix, chopped glass, 296 K	7,000–14,000	(2)
		Woven cloth, 296 K	7,000–21,000	(2)
		Woven cloth, 366 K	4,600	(2)
		Woven cloth, 394 K	3,000	(2)
		Woven cloth, 422 K	1,900	(2)
		Pultruded	11,000	(3, 4)
		SMC, 296 K	7,000–15,000	(2)
		SMC, low pressure, 296 K	7,000–150,000	(2)
		BMC, TMC, 296 K	10,000–12,000	(2)
		EMI shielding (conductive), 296 K	9,700–10,000	(2)
Impact strength, Izod	$J\,m^{-1}$	Cast, rigid	11–21	(2)
		Cast, flexible	>370	(2)
		Glass fiber-reinforced	80–1,600	(2)
		EMI shielding (conductive)	270–640	(2)
Hardness	Rockwell	Glass-reinforced	M50	(6)
	Barcol	Glass fiber-reinforced	40–80	(2)
	Barcol	EMI shielding (conductive)	45–50	(2)
	Barcol	Cast, rigid	35–75	(2)
	Shore	Cast, flexible	D84–94	(2)
	Barcol	Blend (flexible : rigid = 30 : 70)	0–5	(5)
	Barcol	Blend (flexible : rigid = 20 : 80)	20–25	(5)
	Barcol	Blend (flexible : rigid = 10 : 90)	30–35	(5)
	Barcol	Blend (flexible : rigid = 5 : 95)	35–40	(5)

*SMC = sheet molding compounds; BMC = bulk molding compounds; TMC = thick molding compounds; EMI = electromagnetic interference.

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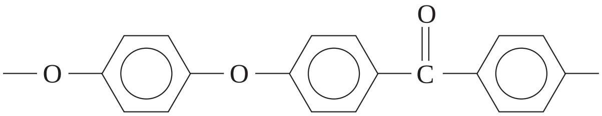
Poly(ether ether ketone)

J. R. FRIED

ACRONYM, TRADE NAME PEEK, Victrex® (ICI)

CLASS Polyketones

STRUCTURE



MAJOR APPLICATIONS General-purpose molding and extrusion polymer for high-performance applications, especially as resin for carbon fiber composites. Examples include chemical resistant tubing and electrical insulation, automotive bearings, pump and valve construction for corrosive applications, and compressor valve plates.

PROPERTIES OF SPECIAL INTEREST Good abrasion resistance; low flammability and emission of smoke and toxic gases; low water absorption; resistance to hydrolysis, wear, solvents, radiation, and high-temperature steam; ease of processing and excellent thermal stability and mechanical properties at high temperatures.

TYPE OF POLYMERIZATION Nucleophilic displacement of activated aromatic halides in polar solvents by alkali metal phenates or Friedel–Crafts processes; examples include polycondensation of the potassium salt of hydroquinone and 4,4′-difluorobenzophenone in DMSO at temperatures up to 340°C and the polycondensation of 4,4′-difluorobenzophenone and silylated hydroquinone at 220–320°C.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	288.31	–
Solvents	Very low or no solubility in ordinary solvents; concentrated sulfuric acid will dissolve and sulfonate PEEK; at high temperatures, dilute solutions can be obtained in hydrofluoric acid, trifluoromethanesulfonic acid, dichlorotetrafluoroacetone monohydrate, phenol–1,2,4-trichlorobenzene, and benzophenone			
Polymers with which compatible	Poly(ether ketone), poly(ether ether ether ketone), poly(ether ether ketone ketone); polyetherimide			
Characteristic ratio $\langle r^2 \rangle_0 / nl^2$	–	–	3.04	(1)
Compressibility coefficient, isothermal	bar^{-1}	At T_m At 340°C At 360°C At 380°C	9.302×10^{-5} 9.4×10^{-5} 10.2×10^{-5} 11.0×10^{-5}	(2)
Continuous service temperature	K	–	473	(3)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Crystallinity	%	Typical	30–35	(4)
		Maximum	48	
Density	$g\,cm^{-3}$	Amorphous	1.263–1.265	(5, 6, 7)
		Crystalline	1.400–1.401	
Entropy of fusion	$kJ\,K^{-1}\,mol^{-1}$	*PVT* data	0.0758	(2)
		DSC data	0.0951	(5)
Maximum extensibility $(L/L_0)_r$	%	Annealed	42	(8)
		As molded	103	(8)
		ASTM D 638	150	(3)
Flexural modulus	MPa	At 23°C	3,700	(9)
		At 100°C	3,600	
		At 200°C	500	
		At 300°C	300	
Glass transition temperature	K	*PVT* data	425	(2)
		Quenched (DSC)	410	(8)
		Annealed (DSC)	415	(8)
Hardness	R scale	Rockwell	126	(9)
Heat capacity	$kJ\,K^{-1}\,mol^{-1}$	Amorphous, 350 K	0.367	(10)
		Amorphous, 400 K	0.415	
		Amorphous, 610 K	0.600	
		Amorphous, 660 K	0.623	
		32% crystalline, 350 K	0.366	
		32% crystalline, 400 K	0.425	
		32% crystalline, 450 K	0.484	
		32% crystalline, 500 K	0.529	
		32% crystalline, 550 K	0.559	
Heat deflection temperature	K	At 1.81 MPa (D648)	433	(3)
Heat of fusion	$kJ\,mol^{-1}$	–	36.8	(2)
			37.5	(5)
Impact strength	$J\,m^{-1}$	Unnotched Izod	No break	(8)
		Notched Izod (D256)	84	
Index of refraction, n	–	–	1.671	(11)
Maximum use temperature	K	1 h exposure	673	(9)
Melt viscosity	Pa s	At 380°C and 1,000 s^{-1}	100–300	(9)

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Poly(ether ether ketone)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melting temperature	K	DSC Equilibrium	608–616 657–668	(5, 6, 8) (5, 12, 13)
Persistence length	Å	97.4% H_2SO_4, 30°C	54	(14)
Plateau modulus G_N^0	MPa	At 623 K (calculated)	4.0	(15)
Reducing temperature T^*	K	Flory equation of state (0–500 bar)	9,272	(16)
Reducing pressure P	MPa	Flory equation of state (0–500 bar)	726.6	(16)
Reducing volume v^*	$cm^3\ g^{-1}$	Flory equation of state (0–500 bar)	0.6842	(16)
Solubility parameter	$(MPa)^{1/2}$	Calculated	21.2–22.6	(17)
Sub-T_g transition	K	1 Hz (DMTA) 1 kHz (dielectric)	205 239	(18)
Tensile modulus	GPa	D638	3.56	(8)
Tensile strength	MPa	At 23°C At 100°C At 200°C At 300°C	92.0 50 12.0 10.0	(9)
Thermal conductivity	$W\ m^{-1}\ K^{-1}$	C177	0.25	(9)
Thermal expansion coefficient	K^{-1}	$30°C < T < 150°C$ at $P = 0$ Melt	1.610×10^{-4} 6.690×10^{-4}	(2)
Volume resistivity	$W\ cm^{-1}$	23°C	4.9×10^{16}	(9)
Water absorption	%	24 h at 40% RH	0.15	–
WLF parameters: C_1 and C_2	C_1 = None C_2 = K	$T_0 = 412.9$ K	$C_1 = 29.96$ $C_2 = 53.74$	(19)
Yield stress	MPa	D638	91	(3)

Avrami parameters for isothermal crystallization

T_c (K)	n^*	k (s^{-3})	Reference
427.6	2.98	8.9×10^{-11}	(20)
429.6	2.81	7.1×10^{-10}	(20)
432.6	3.07	1.2×10^{-8}	(20)
643	3.4	2.6×10^{-3}	(21)
663	3.6	6.7×10^{-5}	(21)
683	3.8	2.9×10^{-5}	(21)

*At half-life for crystallization.

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PROPERTIES	UNITS	CONDITIONS	VALUE				REFERENCE
Gas evolution, *G* value (10^{-4}) of component gas	—	γ irradiation (under vacuum)	H_2	CO	CO_2	CH_4	(10)
		Amorphous; quenched (7.4 MGy dose)	12	6.5	12	0.20	
		Crystalline (8.1 MGy dose)	6.3	12	5.5	0.14	
		Electron beam					(22)
		Amorphous (6 MGy dose)	12	5.2	16	0.22	
		Crystalline (5.8 MGy dose)	7.5	3.4	11.3	0.16	
Infrared spectrum (principal absorptions)	cm^{-1}	Assignment	Wavenumber				(23)
		In-place vibration of aromatic hydrogens	1,160				
		Asymmetric stretch of diphenyl ether groups	1,227 and 1,190				
		Skeletal in-phase phenyl ring vibration	1,599 and 1,492				
		Carbonyl stretching	1,655				
Permeability *P*	m^3 (STP) m s^{-1} m^{-2} Pa^{-1}	O_2, 7.8% crystallinity	6.2×10^{-16}				(24)
		CO_2, amorphous	6.0×10^{-18}				(25)
		CO_2, 26–30% crystallinity	$2.4 \times 10^{[} - 18$				(25)
Lattice	—	—	Orthorhombic				(4, 26)
Monomers per unit cell	—	—	2/3				(4, 26)
Unit cell dimensions	Å	—	$a = 7.75–7.88$ $b = 5.86–5.94$ c (chain axis) = 9.88–10.07				(4, 26)
Important patent	J. Rose and P. Staniland (assigned to ICI Americas, Inc.) U.S. 4,320,224, 16 Mar. 1982.						

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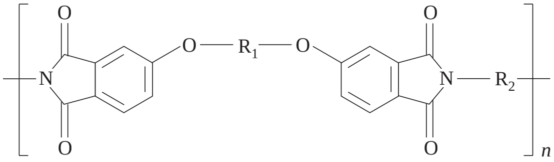
Poly(ether imide)

LOON-SENG TAN

ACRONYM, TRADE NAME PEI, Ultem®

CLASS Polyimides; engineering thermoplastics

STRUCTURE

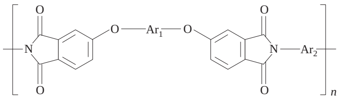


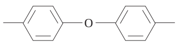
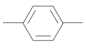
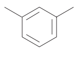
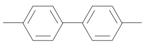
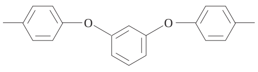
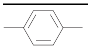
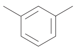
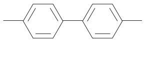
SYNTHESIS Aromatic polyetherimides are usually prepared from (a) bisphenoxide salts and aromatic dinitrobisimides via nucleophilic nitro-displacement reactions[1,2,3]; (b) two-step polycondensation of aromatic diamines and ether-dianhydrides in a polar aprotic solvent, followed by thermal[4] or chemical[5,6] cyclodehydration of the polyamic acid precursors; and (c) one-step, high temperature solution polymerization of aromatic diamines and ether-dianhydrides in a phenolic solvent, removing water of condensation azeotropically.[7] Certain polyetherimides can also be synthesized via direct melt polymerization.[8]

MAJOR APPLICATIONS Printed circuit boards and hard disks for computers, under-the-hood automotive uses, reinforced composites for aerospace applications.

PROPERTIES OF SPECIAL INTEREST Commercial polyetherimide (Ultem) is an amorphous thermoplastic with the following characteristics: high heat resistance, strength, and modulus; inherent flame resistance with low smoke evolution; high dielectric strength, stable dielectric constant and dissipation factor over a wide range of temperature and frequencies; transparency; amenable to conventional molding processes (injection, compression or blow-molding).

Glass-transition and melting (T_m) temperatures* of 4,4′-isomeric polyetherimides†



Ar_1 (BISPHENOLATE)	Ar_2 (BISPHTHALIMIDE)				
					
	515	—	528	—	472 603 (T_m)
	482	—	497	—	403
	502	—	520	—	478 616 (T_m)

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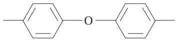
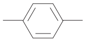
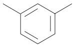
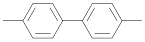
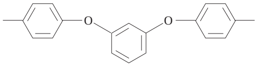
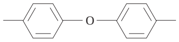
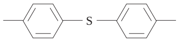
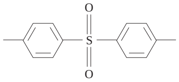
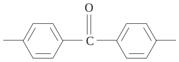
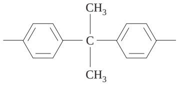
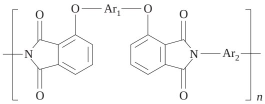
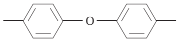
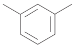
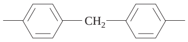
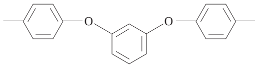
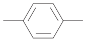
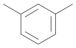
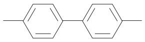
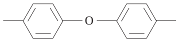
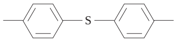
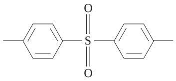
					
	488	–	500	–	457
	485	499[9] 699 (T_m)	482 465[10]	530[9] 755 (T_m)	451
	533	–	538	–	492
	483	–	512	–	467
	496	–	488	–	–

* Temperatures (in K) as determined by DSC.
† Unless otherwise indicated, all the values are from references (2) and (7).

Glass-transition temperatures* of 3,3′-isomeric polyetherimides†



Ar$_1$ (BISPHENOLATE)	Ar$_2$ (BISPHTHALIMIDE)				
					$-(CH_2)_6-$
	536	532	–	487	–
	499	514	–	466	–
	550	548	–	497	–
	512	505	–	471	401
	507	504	–	475	–
	540	539	–	503	–

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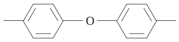
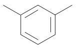
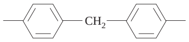
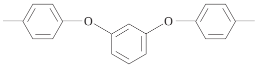
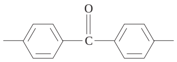
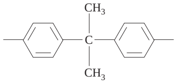
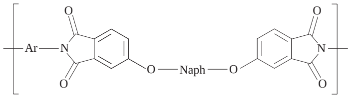
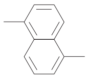
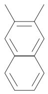
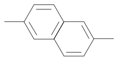
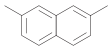
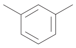
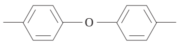
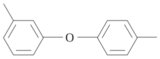
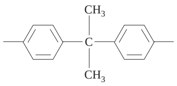
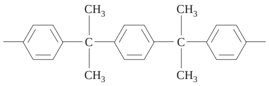
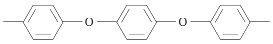
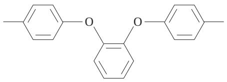
Ar₁ (BISPHENOLATE)	Ar₂ (BISPHTHALIMIDE)				
					$-(CH_2)_6-$
	–	521	–	489	–
	508	509	503	–	408

* Temperatures (in K) as determined by DSC.
† All the values are from references (2) and (7).

Glass-transition and melting (T_m) temperatures* of naphthalene-based polyetherimides[11]



Ar (AMINE)	NAPH [NAPHTHALENE BIS(ANHYDRIDE)]			
				
	533	528	503 613 (T_m)	527
	513	508	522	518
	508	499	498	494
	538	–	509	520
	526	–	519	519
	–	502	–	501
	–	481	–	Not found

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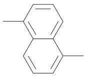
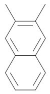
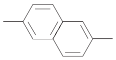
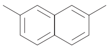
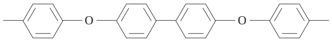
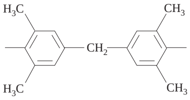
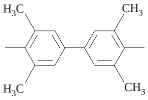
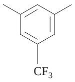
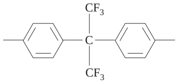
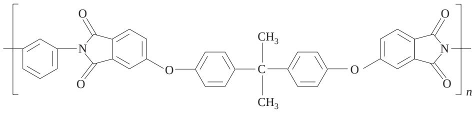
Ar (AMINE)	NAPH [NAPHTHALENE BIS(ANHYDRIDE)]			
				
	–	500	503	504
	554	538	–	545
	Not found	581	–	Not found
	523	523	–	508
	549	529	491	529

* Temperatures (in K) as determined by DSC.

Commercial polyetherimide products

PRODUCT NAMES*	PRODUCT DESCRIPTION
Ultem 1000 series	Unreinforced grades polyetherimide resins 
Ultem 2000 series	Glass reinforced resins (10–40% glass fillers)
Ultem 3000 series	Glass- and mineral-fiber reinforced polyetherimide resins for a balance of low warpage, dimensional stability and low CTE
Ultem 4000 series	Polyetherimide containing internal lubricants
Ultem CRS5000 series	Copolyetherimide with improved chemical resistance
Ultem 7000 series	Carbon reinforced polyetherimide resins
Ultem 8000 and 9000 series aircraft resins	Polyetherimide resins to meet FAR 25.853 regulations for commercial aircraft interiors
Ultem LTX series resins	A PEL/polycarbonate blend with higher impact resistance
Ultem Healthcare (HP) resins	Ultem 1000 resins melt filtered to 40 microns

* Supplier: GE Plastics, Plastics Technology Center, One Plastics Avenue, Pittsfield, Massachussetts 01201, USA.

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Mechanical properties of Ultem 1000

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength	MPa	ASTM D 638; yield, Type I, 3.2 mm	105	(12)
Tensile elongation	%	ASTM D 638; yield, Type I, 3.2 mm	7.0	(12)
Tensile elongation, ultimate	%	ASTM D 638; break, Type I, 3.2 mm	60	(12)
Tensile modulus	MPa ($\times 10^3$)	ASTM D 638; yield, Type I, 3.2 mm	3.0	(13)
Flexural strength	MPa	ASTM D 790; yield, 3.2 mm	150	(12)
Flexural modulus	MPa ($\times 10^3$)	ASTM D 790; yield, 3.2 mm	3.3	(12)
Compressive strength	MPa	ASTM D 695	150	(12)
Compressive modulus	MPa ($\times 10^3$)	ASTM D 695	3.3	(12)
Shear strength	MPa	ASTM D 732	100	(12)
Impact strength, unnotched Izod	$J\,m^{-1}$	ASTM D 256; 3.2 mm, 23°C	1,300	(12)
Impact strength, notched Izod	$J\,m^{-1}$	ASTM D 256; 3.2 mm, 23°C	50	(12)
Gardner impact	J	ASTM D 3029; 23°C	37	(12)
Shear strength, ultimate	MPa	—	90–103	(12)
Rockwell hardness	—	ASTM D 785	109	(12)
Taber abrasion	mg (1,000 cycles)$^{-1}$	ASTM D 1044; CS-17, 1 kg	10	(12)
Poisson's ratio	—	ASTM D638	0.36	(12)

Thermal properties of Ultem 1000

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Vicat softening point, method B	K	ASTM D1525; Rate B	492	(12)
Heat deflection temperature	K	ASTM D648 Unannealed at 0.45 MPa, 6.4 mm	483	(12)
		Unannealed at 1.8 MPa, 6.4 mm	473	(12)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	ASTM C177	0.22	(12)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Coefficient of thermal expansion	10^{-5} K^{-1}	ASTM E831; flow X E-5, from −20 to 150°C	5.6	(12)
Continuous service temperature index	K	UL 756B	443	(13)

Glass-transition and secondary-relaxation temperatures and associated activation energy values of poly(etherimide) (Ultem)*

Test Method/Conditions	T_g (K)	E_a (kJ mol^{-1})	T_β (K)	E_a (kJ mol^{-1})	T_γ (K)	E_a (kJ mol^{-1})	Reference
Torsion pendulum; ~1 Hz	485	–	343	–	168	–	(14)
Forced oscillation dynamic-mechanical analysis; 1 Hz	492	–	355	–	160	–	(15)
Forced oscillation dynamic-mechanical analysis; 1 Hz	501	330–1250	–	–	–	–	(16)
Forced oscillation dynamic-mechanical analysis; 35 Hz	–	–	379	–	186	–	(17)
Dielectric measurement; 1,000 Hz	513	–	–	–	–	–	(16)
Dielectric measurement	–	–	–	–	–	43	(18)

*Adapted from reference (19).

Flammability of Ultem 1000(12)

PROPERTY	UNITS	CONDITIONS	VALUE
UL94V-O flame class rating	mm	UL 94	0.41
UL94-5VA flame class rating	mm	UL 94	1.9
Oxygen index (LOI)	%	ASTM D2863	47
NBS smoke density flaming mode	–	ASTM E662 Flaming, D_s at 4 min	0.7
		Flaming, D_{max} at 20 min	30

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Electrical properties of Ultem 1000[12]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Volume resistivity	ohm m	ASTM D2571; 1.6 mm	1.0×10^{15}	12
Dielectric strength	$kV\,mm^{-1}$	ASTM D149		12
		1.6 mm, in air	33	
		1.6 mm, in oil	28	
		3.2 mm, in oil	20	
Dielectric constant	–	ASTM D150		12
		At 100 Hz,	3.15	
		At 1kHz	3.15	
Dissipation factor	–	ASTM D150		12
		At 100 Hz	0.0015	
		At 1 kHz	0.0012	
		At 2,450 MHz	0.0025	
Arc resistance	s	–	128	13

Physical properties of Ultem 1000

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Specific gravity	–	ASTM D792	1.27	(12)
Mold shrinkage	(m/m)	ASTM D955; flow, 3.2 mm	0.007	(12)
Water absorption	%	ASTM D570	0.25	(12)
		At 24 h, 23°C		
		Equilibrium, 23°C	1.25	(12)
CO_2 permeabilities	barrer*	35°C and 10 atm pressure	1.33	(12)
Permselectivity for CO_2 and CH_4 (a)	–	35°C and 10 atm pressure	36.9	(20)

*1 Barrer = 10^{-10} cm^3(STP) cm/(s cm^2 cmHg), where the standard temperature and pressure (STP) are 273.15 K and 1 atm (1.1013×10^{-5} Pa), respectively.

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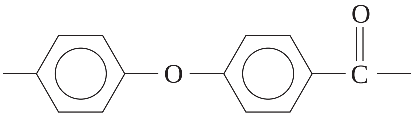
Poly(ether ketone)

J. R. FRIED

ACRONYM, TRADE NAME PEK, Kadel®

CLASS Polyketones

STRUCTURE 

TYPE OF POLYMERIZATION Nucleophilic displacement of activated aromatic halides in polar solvents by alkali metal phenates or Friedel–Crafts processes.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	196.21	–
Density	$g\,cm^{-3}$	Amorphous Crystalline	1.272 1.430	(1) (1, 2)
Maximum extensibility $(L/L_0)_r$	%	–	68	(3)
Impact strength	$J\,m^{-1}$	Notched Izod (D256)	59	(3)
Glass transition temperature	K	DSC	425 427	(1, 3) (2)
Melt flow	$dg\,min^{-1}$	At 400°C	1.5	(1)
Melting temperature	K	DSC	634–640	(1–3)
Tensile impact strength	$kJ\,m^{-2}$	–	168	(3)
Tensile modulus	GPa	D638	3.19	(3)
Tensile strength	MPa	D638	104.0	(3)
Unit cell dimensions	Å	–	$a = 7.63$ $b = 5.96$ c (chain axis) $= 10.0$	(1, 2)

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Poly(ether sulfone)

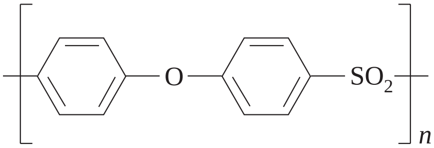
TAREK M. MADKOUR

ACRONYM, TRADE NAMES PES, Victrex 100P and 200P (ICI)

CLASS Poly(ether sulfones)

SYNTHESIS Polycondensation

STRUCTURE



MAJOR APPLICATIONS Medical and household appliances that are sterilizable by hot air and steam such as corrosion-resistant piping. Also used in electric and electronic applications such as television components. Used as membranes for reverse gas streams and gas separation.

PROPERTIES OF SPECIAL INTEREST High performance thermoplastic of relatively low flammability. Amorphous, high-creep resistance and stable electrical properties over wide temperature and frequency ranges. Transparent with good thermal and hydrolytic resistance.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	232.25	—
Infrared bands (frequency)	cm^{-1}	Group assignments		(1, 2)
		SO_2 scissors deformation	560	
		SO_2 symmetric stretch	1,151; 1,175	
		SO_2 asymmetric stretch	1,294; 1,325	
		Aryl-O-aryl C–O stretch	1,244	
		Aromatic CH stretches	3,000-3,200	
Thermal expansion coefficient	K^{-1}	Victrex 200P	5.5×10^5	(3)
		Victrex 430P (30% glass fiber)	2.3	
Density	$g\,cm^{-3}$	Victrex 200P	1.37	(3)
		Victrex 430P (30% glass fiber)	1.60	(3)
Molar volume	$cm^3\,mol^{-1}$	25°C	157	(4)
Solubility parameter δ	$(MPa)^{1/2}$	Calculated, 25°C	23.12	(4)
		Victrex 4800	22.9	(5)
Theta temperature	K	DMF/methanol (83/17)	298	(6)
		DMF/toluene (39/61)	303	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature	K	Forced oscillation dynamic-mechanical analysis	498	(7)
Sub-T_g transition temperature	K	γ-relaxation temperature	193	(7)
Heat capacity	$kJ\,K^{-1}\,mol^{-1}$	–	0.174	(8)
Heat deflection temperature	K	(1.82 MPa)	507	(9)
		30% glass fiber reinforced	476	
		30% carbon fiber reinforced	507	

Mechanical properties[3,9,10]

Property	Units	Resin		
		Neat resin	30% glass fiber reinforced	30% carbon fiber reinforced
Tensile modulus	MPa	2,413	–	–
Tensile strength	MPa	82.8	146.9	211.7
Maximum extensibility $(L/L_0)_r$	%	40–80	2.57	1.11
Flexural modulus	MPa	2,552	6,987	13,973
Flexural strength	MPa	128	210	264
Notched Izod impact strength	$J\,m^{-1}$	85.7	296	88
Unnotched Izod impact strength	$J\,m^{-1}$	–	1,082	521
Hardness	Shore D	88	86	89

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
WLF parameters: C_1 and C_2	–	–	70.98 241.2	(11)
Refractive index n	–	20°C	1.545	(12)
Dielectric constant	–	–	3.5	(13)
Resistivity	ohm cm	–	1×10^{17}	(3)
Speed of sound, longitudinal	$m\,s^{-1}$	–	2,260	(14)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Permeability coefficients	m^3 (STP) m s^{-1} m^{-2} Pa^{-1}	50°C and pressure difference of 10 bar		(15)
		Gas		
		He	7.95×10^{-17}	
		CO_2	3.15×10^{-17}	
		O_2	6.0×10^{-18}	
Thermal conductivity k	W m^{-1} K^{-1}	–	0.18	(13)
Maximum use temperature	K	–	491	(13)
Water absorption	%	24 h	0.43	(3)

Dual-mode parameters[16]

Gas	Sorption parameters			Diffusion coefficients	
	K_D [m^3 (STP) m^{-3} atm^{-1}]	C'_H [m^3 (STP) m^{-3}]	b (atm^{-1})	$D_D \times 10^{12}$ (m^2 s^{-1})	$D_H \times 10^{12}$ (m^2 s^{-1})
CO_2	0.807	16.310	0.398	2.792	0.441
C_2H_6	0.496	10.844	0.289	–	–
CH_4	0.240	6.445	0.109	0.151	0.128

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Poly(ethyl acrylate)

JIANYE WEN

ACRONYM PEA

CLASS Vinyl polymers

STRUCTURE $[-CH_2-\underset{\displaystyle COOC_2H_5}{\underset{|}{C}H}-]$

MAJOR APPLICATIONS Coatings, textiles finishing, paper saturants, leather finishing, and oil-resistant and high-temperature-resistant elastomers.

PROPERTIES OF SPECIAL INTEREST A rubberlike, considerably softer, and more extensible polymer compared to poly(methyl acrylate); has superior resistance to degradation and shows remarkable retention of its original properties under use conditions.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	25°C	1.12	(1–3)
Glass transition temperature	K	Inherent viscosity = 0.05 g polymer in 100 ml toluene		
		0.25	231	(4)
		0.6	230	(4)
		0.9	238	(4)
		5.0	246	(4)
		7.0	245	(4)
		Conventional	249	(2, 4–7)
		Syndiotactic	249	(3, 8)
		Isotactic	248	(9, 10)
Heat capacity	$KJ\,K^{-1}\,mol^{-1}$	−183°C	0.0579	(11)
		−73°C	0.1030	
		27°C	0.1787	
		227°C	0.2219	
		ΔC_p	4.560/10.021	
Interaction parameter χ	–	Butane, 70–90°C	1.318–1.232	(12)
		Hexane, 70–110°C	1.483–1.296	
		Heptane, 70–110°C	1.585–1.345	
		Decane, 70–110°C	1.926–1.645	
		Cyclohexane, 70–110°C	1.148–0.974	
		Benzene, 70–110°C	0.183–0.188	
		Toluene, 70–100°C	0.289–0.301	
		Chloroform, 70–110°C	−0.478 to −0.322	
		Carbon tetrachloride, 70–110°C	0.384–0.365	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Interaction parameter χ	—	Acetone, 70–110°C	0.507–0.411	(12)
		Methyl ethyl ketone, 70–110°C	0.400–0.218	
		Tetrahydrofuran, 70–100°C	0.215–0.191	
		Dioxane, 70–100°C	0.239–0.255	
		Methyl acetate, 70–110°C	0.402–0.394	
		Ethyl acetate, 70–110°C	0.365–0.363	

Mark-Houwink parameters: *K* and *a*

Solvent	Temp. (°C)	Mol. wt. range ($M \times 10_4$)	$K \times 10^3$ (ml g^{-1})	*a*	Reference
Acetone	25	−450	51	0.59	(13)
Acetone	30	−50	20.0	0.66	(14)
Benzene	30	−67	27.7	0.67	(15)
Butanone	30	−700	2.68	0.80	(16)
Chloroform	30	−54	31.4	0.68	(15)
Ethyl acetate	30	−54	26.0	0.66	(15)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength	MPa	—	0.2	(17, 18)
Elongation at break	%	—	1,800	(17, 18)
Refractive index n_D^{25}	—	—	1.464	(19)
Second virial coefficient	$A_2 \times 10^4$ mol cm^3 g^{-2}	Acetone		
		20°C, $M \times 10^4 = 5.5$–86	5.0–3.1	(20)
		28°C, $M \times 10^5 = 3.2$–80	10.52	(21)
		30°C, $M \times 10^5 = 1.45$–1.91	14.6	(22)
Solubility parameter	(MPa)$^{1/2}$	—	19.3	(23)
Solvents	Aromatic hydrocarbons, chlorinated hydrocarbons, tetrahydrofuran, esters, ketones, methanol, butanol, glycol ether			(24)
Nonsolvents	Aliphatic hydrocarbons, hydrogenated naphthalenes, diethyl ether, aliphatic alcohols ($C > 5$), cyclohexanol, tetrahydrofurfuryl alcohol			(24)
Surface tension	mN m^{-1}	$M_w = 2.8 \times 10^4$		(25)
		20°C	37.0	
		150°C	27.0	
		200°C	23.2	
	mN m^{-1} K^{-1}	$-d\gamma/dT$	0.070	
	χ^p	Polarity	0.174	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Thermal conductivity I	$W m^{-1} K^{-1}$	310.9 K	0.213	(26)
		422.1 K	0.230	
		533.2 K	0.213	
Theta solvent	—	*n*-Butanol	44.9°C	(27)
		Ethanol	37.4°C	
		Methanol	20.5°C	
		n-Propanol	39.5°C	

Unperturbed dimension*

Conditions	$r_0/M^{1/2} \times 10^4$ (nm)	$r_0/M^{1/2} \times 10^4$ (nm)	$\sigma = r_0/r_{0f}$	$C_\infty = r_0^2/nl^2$	Reference
Acetone; methanol, 30°C	720 ± 30	308	2.34 ± 0.10	10.9	(28)
Acetone, 25°C	856	308	2.78	15.4	(16)
Undiluted, 60°C	$d \ln r_0 2/dT = -0.2 \times 10^{-3}$ [deg^{-1}]	—	—	—	(29)

*See references (19, 30, 31) for details.

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Polyethylene, elastomeric (very highly branched)

A. PRASAD

ACRONYM, ALTERNATIVE NAMES POE, polyolefin elastomer, ultra-low-density ethylene copolymer

CLASS Poly(α-olefins)

STRUCTURE $-[CH_2{-}CH_2{-}CHR{-}CH_2]_n-$ (R = α-olefin)

MAJOR APPLICATIONS POE is a new family of ethylene α-olefin copolymers produced using metallocene catalyst. The uncross-linked polymers referred to in this chapter are known to have only moderate elastomeric recovery properties (up to 96%). These copolymers are characterized by a narrow molecular weight distribution (MWD) ($M_w/M_n = 2$–2.5) and homogeneous comonomer distribution.[1–12] The control of chain microstructure by the use of metallocene catalyst makes it possible to produce poly(α-olefin) copolymers with considerably lower density, which has not been possible before using the conventional Ziegler-Natta catalyst. Some of the highly branched ethylene copolymers presented in the entry on *Polyethylene, metallocene linear low-density*, in this handbook may be closely related.

Engage® POE, an octene-1 copolymer, is now commercially available in wide variety of melt indexes and density ranges (over 18 grades) from Dow Chemical Company produced using Dow's proprietary single-site, constrained geometry catalyst (Insite) technology.[3,6] Engage POEs are known to have small amounts of long chain branching (LCB) to improve processibilty.[12] Some butene-1 and hexene-1 copolymers of density lower than 0.880 g cm^{-3} made by the Exxon's metallocene catalyst are also known to exhibit moderate elastomeric properties.[7]

The moderate elastomeric properties in these ethylene copolymers have been attributed to the high fractional volume of amorphous phase anchored at multiple points to the minor crystalline domain on the same chains akin to a cross-linked system.[1,3–5,7,9,10] At present, POEs are being actively studied in academic and industrial laboratories. Consequently, only limited data is available in the open literature. Properties listed below are intended to represent best published examples of the most commonly available commercial grades of POEs in the density range of 0.863 to 0.885 g cm^{-3}.

POEs have been used in both plastic and rubber applications. These elastomeric polyethylenes have ability to be cross-linked via peroxide, irradiation, and moisture (if silane grafted). Potential applications include tubing, impact modifiers, low-voltage cable insulation, elastic films, foams, shoe soles, belts, automotive hoses, medical applications, gasket seals, and other electrical applications.

PROPERTIES OF SPECIAL INTEREST Modulus/flexibility, elasticity, toughness, processibility, excellent optics and electrical properties, superior heat resistance, and UV stability over cross-linked rubbers such as EPDM and EPM, low brittleness temperature, good chemical resistance to common solvents, and good heat seal.

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Polyethylene, elastomeric (very highly branched)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melt index	$g\ (10\ min)^{-1}$	D 1238	0.5–30.0+	(6)
Density range	$g\ cm^{-3}$	D 792 (commercial resins)	0.863–0.885	(6)
Mooney viscosity range	—	D 1646, ML 1 + 4 at 394 K	<5–35	(6)
Total SCB	mol%	Not specified	4.7–13.6	(3, 4, 13)
Glass transition temperature	K	DSC, density = $0.8717\ g\ cm^{-3}$ (12 mol% octene-1)	221	(13)
		DMA	224	(3)
		DMA, tan δ peak at 1 Hz, density range = $0.880–0.885\ g\ cm^{-3}$ (butene-1)	244–239	(7)
Melting temperature	K	DSC (broad melting range from 253–363 K), peak endotherm values	322–349	(3, 4, 6–8, 10, 14)
Crystallinity	%	DSC	9–21	(3, 4, 7, 8, 10, 13)
Heat of fusion	$kJ\ mol^{-1}$	DSC	0.35–1.1	(3, 4, 7, 8, 10)
Lamella thickness	Å	SAXS	32–53	(9–11)
Avrami exponent	—	DSC and microscopy, octene-1: 46 $CH_3/1{,}000\ C$ Isothermal crystallization temperature range:		(11)
		319-325 K	2.0	
		327-334 K	1.0	
Tensile modulus	MPa	D 1708, quenched		
		Octene-1, density = $0.8702\ g\ cm^{-3}$	7.0	(3)
		$25\ mm\ min^{-1}$ draw	12.5	(5)
		D 412, $5\ mm\ min^{-1}$ draw, (octene-1, density range = $0.856–889\ g\ cm^{-3}$)	1.5–12.5	(2)
Yield stress	MPa	D 1708, quenched (octene-1, density = $0.8702\ g\ cm^{-3}$)	None detected	(3)
1% Secant modulus	MPa	D 790 (butene-1, density = $0.885\ g\ cm^{-3}$)	32–35	(7)
2% Secant modulus	MPa	D 790, density = $0.8717\ g\ cm^{-3}$ (12 mol% octene-1)	14.8	(13)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength at break	MPa	D 638M, 50 mm min^{-1}	9–30	(5, 6)
Elongation at break	%	D 638M, 50 mm min^{-1}	750–>1,000	(5, 6)
Tensile strain recovery	%	25.4 cm min^{-1}, butene-1		(7)
		28% strain	100	
		70% strain	96	
		143% strain	89	
Permanent tension set	%	4th pull, 100% strain	5–35	(5)
Dynamic compression set	%	D 395B, at 20 Hz, 20% strain, 12,000 cycles at 296 K, density = 0.87–0.885 g cm^{-3}	4.5–5.75	(8)
Hysteresis loss	%	12,000 cycles at 296 K, density range = 0.87–0.885 g cm^{-3}	8–11	(8)
		Peroxide cross-linked (4 pph) at 393 K	1–4	
Hardness	^{0}Shore	D 2240, Shore A	66–79	(6, 13)

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Poly(ethylene imine)

TAREK M. MADKOUR

ACRONYM PEI

CLASS Polyamines

STRUCTURE $[-CH_2-CH_2-NH-]_n$

MAJOR APPLICATIONS PEI offers potential cosmetic uses and new directions for clear antidandruff hair products and antiperspirants. Also used as a wet-strength agent in the paper-making process, a flocculating agent with silica sols, and in the coating of composite hollow-fiber membranes.

PROPERTIES OF SPECIAL INTEREST A special highly branched poly(ethylene amine). A cationic surfactant with natural affinity for hair and skin. A chelating agent with the ability to complex with heavy metal salts such as zinc and zirconium salts.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	g mol^{-1}	—	43.07	(1)
Degree of branching	%	Primary amine groups Secondary amine groups Tertiary amine groups	30 40 30	(2)
Molecular weight range	g mol^{-1}	Ring opening polymerization	600–70,000	(1)
Typical polydispersity range (M_w/M_n)	—	Ring opening polymerization	1.9–56.8	(3)
Heat of polymerization	kJ mol^{-1}	—	−83.7	(4)
Density	g cm^{-3}	Low mol. wt. PEI at 20°C Mol. wt. (g mol^{-1}) 60.1 103.1 146.2 189.2	 0.8994 0.9586 0.9839 0.9994	(1)
Mark-Houwink parameters: K and a	K = ml g^{-1} a = None	25°C, 0.1 M Na $1 \times 10^3 < M_w < 2 \times 10^4$ $2 \times 10^4 < M_w < 3 \times 10^6$	K a 2.32 0.14 0.075 0.43	(5, 6)
pH	—	Commercial form	11–12	(4)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Characteristic ratio $\langle r^2 \rangle_0 / nl^2$	—	Calculated at 27°C for the isotactic polymer	6.21	(7)
		For the syndiotactic polymer	6.56	
Temperature coefficient $d \ln \langle r^2 \rangle / dT$	K^{-1} ($\times 10^3$)	Calculated theoretically for the isotactic polymer	1.93	(7)
		For the syndiotactic polymer	2.85	

Unit cell dimensions[1]

Isomer	Lattice	Monomers per unit cell	Cell dimension (Å)			Cell angle (degrees)	Density ($g\ cm^{-3}$)
			a	*b*	*c*	β	
Anhydrate	Ortho	40	29.8	17.2	4.79	Double	1.165
Hemihydrate	Mono	8	10.89	9.52	7.31	127.6	1.152
Sesquihydrate	Mono	8	11.55	9.93	7.36	104.5	1.139
Dihydrate	Mono	4	13.26	4.61	7.36	101.0	1.190

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melting point	K	Mol. wt. ($g\ mol^{-1}$)		(1)
		60.1	284	
		146.2	285	
		404.7	331	
Boiling point	K	Mol. wt. ($g\ mol^{-1}$)/mbar		(1)
		60.1/1,013	389.5	
		103.1/1,013	480.1	
		146.2/1,013	550.9	
		189.2/1,013	606	
		318.5/11	382–383	
		404.7/1	472–473	
Cationic charge density	milli-equiv g^{-1}	—	20	(4)
Refractive index *n*	—	25°C, mol. wt. = 404 $g\ mol^{-1}$	1.5161	(1)
Maximum adsorbtion on pulp fiber	mg g^{-1}	pH = 6, $M_w = 6 \times 10^5$	0.67	(8)
Adsorption equilibrium constant	g l^{-1}	—	3.5	(8)
Free energy of adhesion	kJ mol^{-1}	—	0.191	(8)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Maximum sorption	%	60 min on virgin hair	1.25	(4)
		Low mol. wt. on damaged hair	1.5	
		High mol. wt. on damaged hair	3.4	
Optimum flocculation dosage	equiv l^{-1}	PEI	6.0×10^{-4}	(9)
		PEI:HCl (1:1)	3.0×10^{-4}	
		PEI:HCl (4:1)	4.0×10^{-4}	
Maximum use temperature	K	–	523	(2)
Toxicity (LD50)	g kg^{-1}	–	3	(4)

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Polyethylene, linear high-density

LEO MANDELKERN AND RUFINA G. ALAMO

ACRONYMS, TRADE NAMES PE, HDPE, LPE

CLASS Poly(α-olefins)

STRUCTURE $-CH_2-CH_2-$ poly(ethylene) or $-CH_2-$ poly(methylene)

PREPARATIVE TECHNIQUES Type of polymerization: coordination polymerization.

TYPICAL COMONOMERS Alkenes, vinyl acetate, methacrylates, acrylates, methacrylic acid, acrylic acid.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular mass weight of repeat unit	$g\,mol^{-1}$	Ethylene Methylene	28 14	–
Typical molecular mass range	$g\,mol^{-1}$	Very wide range available	1×10^3–8×10^6	–
Typical polydispersity (M_w/M_n)	–	Very wide range available	1.07 – >10	–

IR (characteristic adsorption frequencies)[1]

Frequency (cm^{-1})	Phase	Transition moment orientation*	Assignment
720	Crystalline	$\parallel$ b-axis	Out-of-phase CH_2 rock of the two chains in the unit cell
	Amorphous	$\perp$ b-axis	CH_2 rock $(tttt)_n$, $n > 4$
731	Crystalline	$\parallel$ a-axis	In-phase CH_2 rock of the two chains in the unit cell
888	Amorphous	$\parallel$	CH_2 rock
1,050	Crystalline	$\parallel$	CH_2 twist
1,078	Amorphous	$\perp$	Skeletal C–C stretch (g and t conformation)
1,176	Crystalline	$\parallel$	CH_2 wag
1,303	Amorphous	$\parallel$	CH_2 wag (gtg conformation)
1,353	Amorphous	$\parallel$	CH_2 wag (gg conformation)
1,368	Amorphous	$\parallel$	CH_2 wag (gtg conformation)
1,463	Crystalline	$\parallel$ b-axis	CH_2 bend
	Amorphous	–	CH_2 bend
1,473	Crystalline	$\parallel$ a-axis	CH_2 bend
1,820	Crystalline	$\parallel$	Combination of 1,100 or 1,130 + 720, 730 (weak)
1,894	Crystalline	$\perp$	Combination of CH_2 rock. 1,168 + 720, 730 (weak)
2,016	Both	$\parallel$	Combination of 1,294 + 720, 730 (weak)
2,150	Both	$\perp$	Combination of CH_2 1,440 + 720, 730 (weak) or 1,100 + 1,050
2,850	–	–	CH_2 symmetric stretch
2,918	–	–	CH_2 asymmetric stretch

*With respect to uniaxial stretch.

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PROPERTY	UNITS	CONDITIONS	VALUE			REFERENCE
NMR (solution)	T_1 = s		T_1	τ_c		
T_1 relaxation time τ_c correlation time ^{13}C	τ_c = ns	1,2,4-Trichlorobenzene, 383 K	2.52	0.019		(2)
		o-Dichlorobenzene, 373 K	2.70	0.018		(3)
		o-Dichlorobenzene, 303 K (extrapolated)	1.24	0.040		(3, 4)
NMR (melt), ^{1}H-chemical shift $-(CH_2)_n-$	ppm	Reference peak: TMSi 220 MHZ	1.3			(5, 6)
NMR (solid, state), ^{13}C chemical shifts	ppm	Melt crystallized, reference peak: TMSi and solid adamantane 50 MHz, 4.7 *T*	Crystalline component = 32.9 Liquid-like component = 31.1			(7)
^{1}H dipolar-decoupled, ^{13}C chemical shifts	ppm	Uniaxially oriented films, $M_v = 3.8 \times 10^5$, reference peak: TMSi and solid adamantane 50 MHz, 1.4 *T*	Crystalline component = 11.8 Liquid-like component = 32.6			(8)
Spin relaxation times	As indicated	Uniaxially oriented films, $M_v = 3.85 \times 10^5$, reference peak: TMSi and solid adamantane 50 MHz, 1.4 *T*	Crystalline component = 1,100 s, 60.5 s, 5 s Liquid-like component = 370 ms, 34 μs			(8)
^{1}H dipolar-decoupled, MAS pulse, ^{13}C NMR, chemical shifts	ppm	Melt crystallized, reference peak: TMSi and solid adamatane 50 MHz, 4.7 *T*	Crystalline component = 33 Liquid-like component = 31 Interfacial component = 31.3			(9)
Spin relaxation times	s		T_{1H}	T_{1C}	T_{2C}	(9)
		Crystalline component, melt crystallized, $M_v = 3 \times 10^6$ (unfractionated), T_c = 403 K, 4 weeks	1.87	2,560, 263, 1.7	–	
	As indicated	Liquid-like component, melt crystallized, $M_v = 3 \times 10^6$ (unfractionated), T_c = 403 K, 4 weeks	0.39 s	0.37 s	2.4 ms	
	As indicated	Interfacial component, melt crystallized, $M_v = 3 \times 10^6$ (unfractionated), T_c = 403 K, 4 weeks	1.61 s	0.37 s	0.044 ms	

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PROPERTY	UNITS	CONDITIONS	VALUE			REFERENCE
			T_{1H}	T_{1C}	T_{2C}	(9)
	s	Melt crystallized, $M_v = 2.48 \times 10^5$ (fraction), $T_c = 402$ K, 23 days				
		Crystalline component	2.20	2,750, 111, 1.3	–	
		Liquid-like component	0.50	0.41	–	
		Interfacial component	2.04	0.41	–	
	s	Solution crystallized, $M_v = 9.1 \times 10^4$ (fraction), $T_c = 358$ K, 0.08 w/v% in toluene				
		Crystalline component	1.90	220, 21, 2	–	
		Interfacial component	1.9	0.46	–	
Thermal expansion coefficient	$^\circ C^{-1}$	Liquid state (t in °C) 130–207°C	$\alpha_l = (0.727 \times 10^{-3}) - (0.030 \times 10^{-5})t - (0.0120 \times 10^{-7})t^2 + (0.0021 \times 10^{-9})t^3$			(10)
		140°C	$\alpha_l = 7.151 \times 10^{-4}$			
	K^{-1}	Crystalline state (semicrystalline) (T in K)	$\alpha_c = (1.734 \times 10^{-3}) + (6.523 \times 10^{-6})T$			(11)
		293–383 K (orthorbombic unit cell)	$\alpha_c = 3 \times 10^{-4}$			
		298 K	$\alpha_c = 2.10 \times 10^{-4}$			
Compressibility coefficient	bar^{-1}	Liquid state, 413–473 K (t in °C)	$(0.894/1{,}767)e^{(4.661 \times 10^{-1})}t$			(11)
		Crystalline state, 293–383 K (t in °C)	$0.0894/(4{,}758 - 22.7t)$			
Density	$g\,cm^{-3}$	Liquid state, 403–480 K (t in °C)	$\beta_l = 0.8674 - (0.0631310^{-2})t + (0.00367 \times 10^{-4})t^2 - (0.00055 \times 10^{-6})t^3$			(10)
Reducing variables	–	(A) From Simha-Somcynsky	–			(11–13)
		(B) From Flory-Orwoll-Vrij				(10, 14)
		(C) From Sanchez-Lacombe				(15, 16)
Reducing temperatures	K	A: 413–473 K, 0–200 MPa	9,250			(11)
		A: 423–476 K, 0–200 MPa	10,046			(11)
		A: 415–473 K, 0–200 MPa	9,772			(11)
		B: 413 K, 0–3.55 MPa	7,300			(10)
		C: 408–471 K, 0–100 MPa	649			(16)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Reducing pressure	MPa	A: 413–473 K, 0–200 MPa	897	(11)
		A: 423–476 K, 0–200 MPa	716	(11)
		A: 415–474 K, 0–200 MPa	748	(11)
		B: 413 K, 0–3.55 MPa	460	(10)
		C: 408–471 K, 0–100 MPa	358	(16)
Reducing volume	$cm^3 g^{-1}$	A: 413–473 K, 0–200 MPa	1.129	(11)
		A: 423–476 K, 0–200 MPa	1.155	(11)
		A: 415–473 K, 0–200 MPa	1.142	(11)
		B: 408–471 K, 0–100 MPa	1.127	(10)
Solvents	Solubility only above 353 K. Hydrocarbons, halogenated hydrocarbons and aromatics, higher aliphatic esters, ketones, di-*n*-amyl ether			—
Nonsolvents	All common solvents below 353 K. Most polar organic solvents even at elevated temperatures, inorganic solvents			—
Solubility parameters	$(MPa)^{1/2}$	Calculated	16.0, 16.8	(17)
		Calculated	16.2	(18)
		Measured	17.1	(19)
Theta temperature Θ	K	Solvent		
		Biphenyl	398	(20)
		Biphenyl	401	(21–24)
		Diphenylene oxide	~391	(20)
		Diphenyl ether	434	(23, 25)
		Diphenyl ether	437	(24)
		Dodecanol-1	411	(26, 23)
		Dodecanol-1	417	(22)
		n-Octyl alcohol	453	(21, 24)
		n-Octyl alcohol	458	(23)
		n-Decyl alcohol	427	(21, 23, 24)
		n-Lauryl alcohol	411	(21, 24)
		p-Tertiary amyl alcohol	472	(21, 24)
		p-Octyl phenol	448	(21, 24)
		p-Nonyl phenol	436	(21, 24)
		2-Ethyl hexyl sebacate	423	(20)
		2-Ethyl hexyl adipate	443	(26)
		3,5,5-Trimethyl hexyl acetate	394	(22)
		Anisole	427	(21, 24)
		Benzyl phenyl ether	465	(21, 24)
		Nitrobenzene	>473	(20)
		Di-butyl phthalate	>473	(20)
		n-Pentane	~358	(27)
		n-Hexane	407, 437	(27)
		n-Octane	504, 489	(28)
		Diphenyl methane	415	(21, 24)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Interaction parameter χ	—	Solvent, Temp. (K)		
		cis-Decahydronapthalene, 419	0.08	(29)
		cis-Decahydronapthalene, 426	0.06	(29)
		trans-Decahydronapthalene, 419	0.06	(29)
		trans-Decahydronapthalene, 426	0.05	(29)
		n-Decane, 419	0.32	(29)
		n-Decane, 426	0.31	(29)
		n-Decane, 418–463	0.18	(30)
		n-Decane, 458	0.12	(31)
		2,4-Dimethyl hexane, 419	0.39	(29)
		2,4-Dimethyl hexane, 426	0.36	(29)
		2,5-Dimethyl hexane, 419	0.43	(29)
		2,5-Dimethyl hexane, 426	0.38	(29)
		3,4-Dimethyl hexane, 419	0.32	(29)
		3,4-Dimethyl hexane, 426	0.30	(29)
		n-Dodecane, 419	0.29	(29)
		n-Dodecane, 426	0.28	(29)
		Ethyl benzene, 419	0.37	(29)
		Ethyl benzene, 426	0.37	(29)
		Mesitylene, 419	0.29	(29)
		Mesitylene, 426	0.27	(29)
		3-Methyl hexane, 419	0.42	(29)
		3-Methyl hexane, 426	0.39	(29)
		2-Methyl heptane, 419	0.39	(29)
		2-Methyl heptane, 426	0.39	(29)
		3-Methyl heptane, 419	0.37	(29)
		3-Methyl heptane, 426	0.36	(29)
		n-Nonane, 419	0.35	(29)
		n-Nonane, 426	0.33	(29)
		n-Octane, 419	0.37	(29)
		n-Octane, 426	0.35	(29)
		1,2,3,4-Tetrahydronapthalene, 419	0.33	(29)
		1,2,3,4-Tetrahydronapthalene, 426	0.32	(29)
		1,2,3,4-Tetrahydronapthalene, 383	0.32	(32)
		Toluene, 419	0.39	(29)
		Toluene, 426	0.40	(29)
		2,2,4-Trimethyl hexane, 419	0.37	(29)
		2,2,4-Trimethyl hexane, 426	0.33	(29)
		2,2,4-Trimethyl pentane, 419	0.41	(29)
		2,2,4-Trimethyl pentane, 426	0.39	(29)
		p-Xylene, 419	0.32	(29)
		p-Xylene, 426	0.32	(29)
		m-Xylene, 419	0.34	(29)
		m-Xylene, 426	0.34	(29)

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Second virial coefficient	mol cm^3 g^{-2} $\times 10^4$	Solvent, Temp. (K), $M_w \times 10^{-5}$			
		1-Chloronaphthalene, 398, 1.10–21.6	12.0–0.78		(33)
		1-Chloronaphthalene, 398, 1.75	10.0		(34)
		1-Chloronaphthalene, 398, 1.44	8.6		(34)
		1-Chloronaphthalene, 398, 0.5–5.6	12.4–2.7		(35)
		1-Chloronaphthalene, 408, 1.20	4.0		(36)
		1-Chloronaphthalene, 408, 0.14–1.20	15.9–10.3		(30)
		Diphenyl methane, 415, 0.82–0.89	−0.25–0.93		(36)
		n-Decane, 388, 1.44	5.9		(34)
		1,2,4-Trichlorobenzene, 408, 0.94	20.6		(36)
		1,2,4-Trichlorobenzene, 413, 0.11–0.20	45.2–41.1		(37)
		1,2,3,4-Tetrahydronaphthalene, 378, 1.44	21.8		(34)
		1,2,3,4-Tetrahydronaphthalene, 378, 1.25–4.65	23.1–15.9		(38)
		1,2,3,4-Tetrahydronaphthalene, 398, 0.92–2.19	26.8–1.7		(33)
Mark-Houwink parameters: *K* and *a*	As indicated	Solvent, Temp. (K), $M_w \times 10^{-4}$	$k \times 10^2$ (ml g^{-1})	*a*	
		1,2,4-Trichlorobenzene, 408, 0.08–12.3	5.1	0.71	(39)
		1,2,4-Trichlorobenzene, 408, –	5.2	0.69	(26)
		1,2,4-Trichlorobenzene, 408, 0.6–20	5.6	0.70	(40)
		1,2,4-Trichlorobenzene, 408, 0.07–6.9	3.9	0.73	(41)
		Decalin, 408, 0.2–10.0	6.2	0.70	(25, 42)
		Decalin, 408, 0.3–10.0	6.8	0.67	(43)
		Decalin, 408, 0.3–6.4	4.6	0.73	(44)
		Decalin, 408, –	5.3	0.73	(45)
		Decalin, 408, 0.3–11.7	6.2	0.70	(39, 25)
		Diphenyl ether, 434.6, 0.2–10.0	29.5	0.50	(25)
		1-Chloronapthalene, 398, –	14.0	0.58	(46)
		1-Chloronapthalene, 398, 0.5–5.6	4.3	0.67	(35)
		1-Chloronapthalene, 402, –	2.7	0.71	(47)
		1-Chloronapthalene, 402, –	9.1	0.69	(47)
		1-Chloronapthalene, 403, 0.6–20	5.6	0.68	(41)
		Tetralin, 378, 1.3–5.7	1.6	0.83	(38)
		Tetralin, 393, 0.5–10.0	2.4	0.78	(48)
		Tetralin, 393, 0.03–5.5	3.3	0.77	(49)
		Tetralin, 403, 0.04–5.0	4.4	0.76	(50)
		Tetralin, 403, 0.08–2.0	3.8	0.72	(51)
		p-Xylene, 278, 1.3–5.0	1.7	0.83	(38)
		p-Xylene, 278, 0.1–1.2	1.8	0.83	(52)
		3,5,5-Trimethyl hexyl acetate, 394, 0.1–5.8	–	0.55	(22)
		Dodecanol-1, 401, 0.09–5.8	–	0.61	(22)
		Biphenyl, 401, 0.18–5.8	–	0.60	(22)

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PROPERTY	UNITS	CONDITIONS	VALUE			REFERENCE
Huggins constant: k'	–	Solvent, Temp. (K), $M_w \times 10^{-5}$				
		Decalin, 408, 0.1–10.0	0.70			(43)
		1-Chloronaphthalene, 403, 0.07–6.9	0.22–0.72			(41)
		1,2,4-Trichlorobenzene, 403, 0.07–6.9	0.36–0.79			(41)
Characteristic ratio $\langle r^2 \rangle_0/nl^2$	–	Theoretical, 413 K	6.9			(53)
			7.4, 7.6			(54)
		Dodecanol, 411 K	6.7			(23, 25, 53)
		Dodecanol, 401 K	7.1			(24)
		Diphenyl methane, 415 K	6.8			(25)
			7.0			(24)
		1-Chloronapthalene, 413 K	6.8			(25)
		bis-2-Ethyl hexyl adipate, 418 K	10.3			(47)
		Biphenyl , 401 K	7.0			(23)
		Diphenyl ether, 434 K	6.4			(25)
		Diphenyl ether, 437 K	6.8			(24)
		Octanol, 453 K	6.4			(25)
Lattice	–	Most stable, 1 atmosphere	Orthorhombic			(55, 56)
Space group	–	Orthorhombic	Pnam			(55, 56)
Chain conformation	–	Orthorhombic	Planar zig-zag			(55, 56)
Unit cell dimensions	Å		*a*	*b*	*c*	
		Orthorhombic, oriented sheet	7.40	4.93	2.53	(55)
		Orthorhombic, fiber	7.41	4.95	2.55	(56)
		Orthorhombic, powder, melt crystallized	7.40	4.93	2.53	(57)
		Orthorhombic, powder, slow, melt crystallized	7.42	4.95	2.55	(58)
		Orthorhombic, solution, expitaxial	7.48	4.97	2.55	(59)
Unit cell content	–	Orthorhombic	4 CH_2 units			(55, 56)
Lattice	–	Metastable, requires deformation	monoclinic			(60)
Space group	–	Monoclinic	C2 m^{-1}			(60)
Chain conformation	–	Monoclinic	Planar zig-zag			(60)
Unit cell dimensions	Å	Monoclinic	$a = 8.09$, $b = 4.79$, $c = 2.53$			(60)
Unit cell angle	Degrees	Monoclinic	$\beta = 107.9$			(60)
Unit cell content	–	Monoclinic	4 CH_2 units			(60)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Lattice	—	Requires > 3 k bar, near melting point	Hexagonal	(61, 62)
Unit cell dimension	Å	Referred to orthohexagonal axis	$a = 8.46$, $b = 4.88$, $c = 2.45$	(61, 62)
		Referred to hexagonal axis	$a = 4.88$	(61, 62)
Unit cell content	—	Hexagonal	4 CH_2 units	(61, 62)
Degree of crystallinity	%	Depends on molecular weight, crystallization conditions, and method of measurement	35–90	(63–65)
Heat of fusion	$kJ\,mol^{-1}$ (of CH_2 units)	Macroscopic crystal, melting point depression by diluent	4.140	(66, 69)
		Actual finite crystal, depends on molecular weight, crystallization conditions, and method of measurement	1.450–3.730	(63, 65)
Entropy of fusion	$kJ\,K^{-1}\,mol^{-1}$ (of CH_2 units)	Macroscopic ideal crystal, from heat of fusion and equilibrium melting temperature	9.9×10^{-3}	(66–70)
		Actual finite crystal, depends on measured enthalpy of fusion	$3.5–8.9 \times 10^{-3}$	(63–65, 70)
Density (crystalline)	$g\,cm^{-3}$	Orthorhombic unit cell	0.996	(55, 56, 63–65)
		Observed depends on molecular weight and crystallization conditions	0.92–0.99	
Polymorph	—	Stable at atmospheric pressure	Orthothombic	(55, 56)
		Metastable, involves deformation	Monoclinic	(60)
		Pressure > 3 k bar, near melting temperature	Hexagonal	(61, 62)
Avrami exponent	—	M ($g\,mol^{-1}$) = 4,800–5,800, T_c = 125–128°C	4	(64)
		M ($g\,mol^{-1}$) = 7,800–11,500, T_c = 129–128°C	4	(64)
		T_c = 125–128°C	3	(64)
		M ($g\,mol^{-1}$) = $1.4 \times 10^4 - 1.2 \times 10^6$, T_c = 125–132°C	3	(64)
		M ($g\,mol^{-1}$) = $3 \times 10^6 - 8 \times 10^6$, T_c = 125–130°C	2	(64)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature	K	Expansion coefficient	153	(71)
		Expansion coefficient	140	(72)
		Differential scanning calorimetry	150	(72)
		Adiabatic calorimety	148	(73, 74)
		Dynamic mechanical (5 Hz)	150	(72)
		Dynamic mechanical (0.1–1.0 Hz)	146–155	(75)
		Dynamic mechanical 0.67 Hz	140	(76)
		Dynamic mechanical 4.8 Hz	149	(77)
		Dynamic mechanical 10^2 Hz	160	(78)
		Small angle X-ray, expansion coefficient	148	(79)
		Vibrational spectroscopy	< 180	(80)
β-Transition	K	Dynamic mechanical (3.5 Hz)	258 ± 5	(81, 82)
		Dynamic mechanical (0.67 Hz)	253	(83)
		Dynamic mechanical (1 Hz)	253	(84)
		Dynamic mechanical (10^2 Hz)	283	(78)
		Expansion coefficient	243	(85)
α-Transition	K	Dynamic mechanical (3.5 Hz)	303–341	(82)
		Dynamic mechanical (0.1 Hz)	323–383	(75)
		(Value depends on crystallite thickness)		
Equilibrium melting temperature	K	Theoretical	418 ± 1	(86)
		Dilatometry	419	(87)
		Extrapolated, T_m/T_c	419	(88)
		Extrapolated, Gibbs-Thomson	419	(89)
		Extrapolated, Gibbs-Thomson	419	(90–93)
Directly observed melting temperature	K	Depends on molecular weight, crystallization conditions, and method of measurement	391–419	(64, 94)
Heat capacity	$kJ\,K^{-1}\,mol^{-1}$	Experimental 100 K, crystalline	9.45×10^{-3}	(95)
		Experimental, liquid 608 K	43.87×10^{-2}	
		Extrapolated, liquid 300 K	30.89×10^{-2}	
Tensile modulus	MPa	Initial modulus: depends on molecular mass and morphological structure	60–290	(96)
Bulk modulus	—	—	Reciprocal of compressibility	—
Storage modulus	MPa	$T = 298$ K, slow cooled	800	(77)
		$T = 253$ K, $d = 0.936\ g\,cm^{-3}$, 0.67 Hz	600	(83)
		$T = 253$ K, crystallinity 0.40, 1 Hz	400	(75)

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Loss modulus	MPa	$T = 298$ K, slow cooled, 0.67 Hz	6.2		(77)
		$T = 253$ K, $d = 0.936$ g cm^{-3}, 0.67 Hz	7.6		(83)
		$T = 253$ K, crystallinity 0.40, 1 Hz	8.0		(75)
Tensile strength	MPa	Depends on molecular mass, based on original cross-section, strain rate 10^{-1} s^{-1}, $T = 298$ K	10–60		(96)
Yield stress	MPa	Depends on crystallinity level, strain rate 10^{-1} s^{-1}, $T = 298$ K	18–32		(96)
Maximum extensibility (L/L_0)	–	Depends on molecular mass, strain rate 10^{-1} s^{-1}, $T = 298$ K	18–4		(96)
Impact strength	J m^{-1}	Izod (notched), $d = 0.94$–0.97 g cm^{-3}	30–200		(97)
Hardness	Shore D	–	45–70		(98)
Plateau modulus	MPa	378 K	2.2		(99)
		413 K	2.6		(100)
Entanglement molecular weight	g mol^{-1}	378 K	1,100		(99)
		413 K	800		(100)
WLF parameters: C_1 and C_2	–		C_1	C_2	
		$M_v = 2 \times 10^6$ (unfractionated), calculated from ^{13}C NMR correlation times, $T_g = 173$ K $= T_{ref}$	12.5	34.3	(101)
		$M_n = 6 \times 10^5$, $M_w = 4 \times 10^6$, dynamic mechanical, 1 Hz, $T_g = 155$ K $= T_{ref}$			(75)
		Degree of crystallinity = 0.40	15.0	50.5	
		Degree of crystallinity = 0.50	15.4	50.0	
		Degree of crystallinity = 0.70	16.3	48.0	
Abrasion resistance	g MHz^{-1}	Tabor	2–10		(98)
Index of refraction	–	Crystal, $\lambda = 5{,}461$ Å, $T = 298$ K	$\alpha \simeq \beta = 1.520$, $\gamma = 1.582$		(102)
		Amorphous, $\lambda = 5{,}461$ Å			(103)
		$T = 403$ K	1.4327		
		$T = 412.9$ K	1.4297		
		$T = 423.6$ K	1.4261		

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Refractive index increment	$ml\,g^{-1}$	Solvent, Temp. (K)	$\lambda = 436\,nm$	$\lambda = 546\,nm$	
		Biphenyl, 396	–	−0.174	(103)
		Biphenyl, 408	−0.195	−0.172	(104)
		Biphenyl, 400	−0.202	−0.176	(104)
		Bromobenzene, 408	−0.101	−0.089	(104)
		1-Chloronaphtalene, 363	–	−0.198	(42)
		1-Chloronaphtalene, 387–424	–	−0.196–0.194	(105)
		1-Chloronaphtalene, 398	–	−0.195	(42)
		1-Chloronaphtalene, 408	–	−0.190	(42)
		1-Chloronaphtalene, 400	–	−0.191	(106)
		1-Chloronaphtalene, 403	–	−0.193	(107)
		1-Chloronaphtalene, 408	–	−0.193	(108)
		1-Chloronaphtalene, 418	–	−0.196	(107)
		1-Chloronaphtalene, 418	–	−0.188–0.193	(109)
		1-Chloronaphtalene, 418	−0.215	−0.192	(110)
		n-Decane, 384–422	–	0.087–0.099	(105)
		n-Decane, 408	0.117	0.114	(104)
		n-Decane, 379–408	0.116–0.132	0.113–0.126	(111)
		p-Dibromobenzene, 408	−0.179	−0.162	(104)
		o-Dichlorobenzene, 408	−0.091	−0.081	(104)
		o-Dichlorobenzene, 408	−0.095	−0.083	(104)
		Diphenyl methane, 415	−0.146	−0.129	(104)
		1-Dodecanol, 410	0.048	0.046	(104)
		1-Methyl napthalene, 408	−0.206	−0.177	(104)
		Tetrahydronapthalene, 408	−0.087	−0.077	(104)
		Tetrahydronapthalene, 368–417	–	−0.091–0.080	(105)
		1,2,4-Trichlorobenzene, 408	−0.125	−0.192–011	(104, 110)
Surface tension	$N\,m^{-1} \times 10^{-5}$	Pendant drop			
		413 K	28.8		(112, 113)
		453 K	26.5		(112, 113)
		298 K (extrapolated)	35.7		(112, 113)
		423 K	28.1		(114)
		423 K	26.4		(115)
		Wilhelm plate			(116)
		485 K	24.5		
		458 K	26.0		
		293 K (extrapolated)	36.0		
		Maximum bubble pressure, 423 K	22.8		(117)
		Pendant drop, poly(styrene)			(118)
		293 K (extrapolated)	8.6		
		413 K	5.9		
		453 K	5.1		
		Pendant drop, poly(*n*-butyl methacrylate)			(118)
		293 K (extrapolated)	7.1		
		413 K	5.3		
		453 K	4.7		

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Surface tension	$N\,m^{-1} \times 10^{-5}$	Pendant drop, poly(methyl methacrylate)		(118)
		293 K (extrapolated)	11.9	
		413 K	9.7	
		453 K	9.0	
		Pendant drop, poly(ethylene oxide), 423 K	9.5	(115)
		Pendant drop, poly(dimethyl siloxane), 423 K	5.1	(115)
		Pendant drop, poly(tetrahydrofuran), 423 K	4.1	(115)
		Pendant drop, poly(ethylene-vinyl acetate, 423 K	1.3	(115)
		Pendant drop, poly(vinyl acetate),		
		453 K	10.2	(113)
		423 K	9.8	(115)
		413 K	11.3	(113)
		293 K (extrapolated)	14.5	(113)
		Spinning drop, poly(styrene), 473 K	4.4	(119)
		Spinning drop, poly(hexamethylene adipamide), 523 K	10.7	(119)
		Spinning drop, poly(methyl methacylate), 473 K	10.0	(119)
Permeability coefficient P	$cm3^3$ (STP) $cm^{-1}\,s^{-1}\,atm^{-1}$ $(\times 10^{-8})$	Semicrystalline, $d = 0.964\,g\,cm^{-3}$, permeant		(120)
		He, 298 K	0.87	
		O_2, 298 K	0.31	
		Ar, 298 K	1.29	
		CO_2, 298 K	0.28	
		CO, 298 K	0.15	
		N_2, 298 K	0.11	
		CH_4, 298 K	0.30	
		C_2H_6, 298 K	0.45	
		C_3H_4, 298 K	3.06	
		C_3H_6, 298 K	0.88	
		C_3H_8, 298 K	0.41	
		SF_6, 298 K	0.0064	
		H_2S, 293 K	6.5	
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	–	0.52	(121)

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PROPERTY	UNITS	CONDITIONS	VALUE			REFERENCE
Melt viscosity	Pa s	Zero shear, fractions temp. (K)	410 K	465 K	468 K	(122)
		$M_w = 13{,}600$; $M_w/M_n = 1.12$	–	–	2.52	
		$M_w = 19{,}300$; $M_w/M_n = 1.11$	2.57	10.1	–	
		$M_w = 32{,}100$; $M_w/M_n = 1.11$	–	–	28,500	
		$M_w = 33{,}900$; $M_w/M_n = 1.10$	157.0	64.5	–	
		$M_w = 58{,}400$; $M_w/M_n = 1.10$	708.0	28.0	–	
		$M_w = 77{,}400$; $M_w/M_n = 1.19$	1,630.0	64.0	–	
		$M_w = 119{,}600$; $M_w/M_n = 1.18$	–	–	8,000	
		$M_w = 520{,}000$; $M_w/M_n = 1.18$	–	–	28,500	
Coefficient of sliding fraction	–	Sliding on steel				(123)
		Polished	0.60			
		Abraded	0.33			
Speed of sound	m s^{-1}	273 K	1,600			(124)

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Polyethylene, linear low-density

A. PRASAD

ACRONYMS, ALTERNATIVE NAMES LLDPE, low-pressure PE, poly(α-olefin) copolymer

CLASS Poly(α-olefins)

STRUCTURE $-[CH_2-CH_2-CHR-CH_2]_n-$ (R = α-olefin)

INTRODUCTION LLDPE is the common name for copolymers of ethylene with α-olefin comonomer. The comonomers most frequently used commercially are butene, hexene, and octene. Commercial grade LLDPE resins with 4-methyl-1-pentene (4-MP-1) as comonomer is also available. LLDPE prepared by the conventional Ziegler-Natta catalyst system always exhibit high heterogeneity in the intermolecular distribution of comonomer units along the polymer chains.[1–5] The branches are preferentially located in the lower molecular weight chains; thus the bulk of LLDPE behaves as if it were a blend of high molecular weight, linear molecules and low molecular weight, branched molecules. LLDPE differs from LDPE principally through a lack of long-chain branching (LCB) and a narrower molecular weight distribution (MWD).

New types of LLDPEs based on the metallocene catalyst technology have been introduced recently in the market place. Such LLDPEs are characterized by narrower molecular weight and homogeneous short-chain branching distribution.[6–9] Some of the metallocene catalyst based octene-1 LLDPE copolymers made by the Dow Chemical Company are known to have LCB.[9] For the properties of metallocene LLDPE see the entry *Polyethylene, metallocene linear low density*, in this handbook.

LLDPE is commercially available in wide variety of melt indexes (MI) and density ranges. The properties of LLDPE are functions of molecular weight (MW), MWD, density, type, and amount of comonomer.[10–13] The comonomers are also referred to as short-chain branches (SCB). Consequently, physical and mechanical properties also vary accordingly. Mechanical properties such as tensile, tear, and impact are strongly dependent on the chemical nature of the comonomer type. Therefore, it is difficult to list all properties separately. The values of the properties shown in the following table are given in ranges because of their dependence on molecular structure and type of comonomer and are intended to represent the best published examples of the most commonly used commercial grades of LLDPE resins. The physical properties of extruded materials may vary substantially from those of the compression molded materials. For illustration purposes, a few of the physical properties that depend on the chemical nature of the comonomer are presented in Tables 3, 6, and 7.

MAJOR APPLICATIONS Major applications include blown and cast films for bags, shrink-wrap, packaging, and injection molding. Such films exhibit exceptional toughness, dart impact, and puncture resistance when compared to blown films of LDPE. Other applications include blow molding, pipe and conduit, lamination, coextrusion, rotomolding, and wire and cable coatings. There is considerable use of blends of LLDPE with LDPE in a wide variety of applications.

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PROPERTIES OF SPECIAL INTEREST Low cost, flexibility, toughness, high impact strength, low brittleness temperature, good chemical resistance to acids and aqueous solvents, good dielectric properties, good heat seal properties, and much better thermal, stress-crack resistance, and moisture barrier properties when compared to LDPE. The limitations include poor resistance to oxidizing agents; aliphatic, aromatic and polar liquids; and chlorinated solvents. LLDPE is relatively difficult to process by extrusion due to narrower MWD and poor optical clarity when compared to LDPE.

MAJOR SUPPLIERS Equistar Chemicals LP, Dow Chemical Co., Chevron Chemical Co., Du Pont Co., Exxon Chemical Co., Eastman Chemical Co., Union Carbide Corp., Mobil Polymers, Montell Polyolefins, Solvay Polymers, Inc., Novacor Chemicals, Inc.

Catalyst for LLDPE[11,14,15]

POLYMERIZATION PROCESS	CATALYST SPECIFICATION	POLYMERIZATION CONDITION
Gas-phase fluidized bed polymerization, solution polymerization, slurry polymerization, and polymerization in melt under high ethylene pressure	LLDPEs are produced with two broad class of catalysts: (1) Ziegler catalyst: derivative of a transition metal (such as titanium) and organoaluminium compound (such as triethylaluminium) supported on inorganic and organic support (such as silica, magnesium dichloride etc.) (2) Chromium oxide-based catalysts from Phillips Petroleum Co.: these are mixed silica titania support containing 2–20 wt% of titania and a co-catalyst (i.e., trialkylaluminum compounds). These catalysts produce LLDPEs of very broad MWD (M_w/M_n in the range of 12–35) and MI in the 80–200 range	Typical heterogeneous Ziegler catalysts operate at temperature range of 343–373 K and low pressures of 0.1 to 2 MPa in inert liquid medium (e.g., hexane and isobutane) or in the gas phase

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Typical comonomers	—	Butene, hexene, octene, and 4-MP-1	—	(1, 3, 4, 11, 12, 16)
Degree of branching, commercial grades	mol%	D 2238, NMR	2–4	(11)
Typical molecular weight range (M_w)	$g\,mol^{-1}$	GPC, in 1,2,4-trichlorobenzene (TCB) at 408 K	5–20 ($\times 10^4$)	(11)
Typical polydispersity index (M_w/M_n)	—	GPC	4–35	(11)
IR (characteristic absorption frequencies)	cm^{-1}	D 2238	See table below	(17–23)

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Polyethylene, linear low-density

Characteristic IR bands used to identify the type of short-chain branching*

Comonomer type	Methyl deformation band position (cm^{-1})	Methyl rocking band position† (cm^{-1})	Reference
Butene-1	1,379	908, 887, 771(vs)	(17-23)
Hexene-1	1,377.8	908, 894(vs), 837(s), 779(w)	(17-23)
Octene-1	1,377.6	908(vs), 889(s)	(17-23)
4-MP-1	1,383	908, 920(s)	(22)

*See also the entry on LDPE in this handbook.
†vs, s, w refer to the intensities of the absorbance bands: very strong, strong, and weak, respectively.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
NMR	ppm	TCB/d6-benzene solution at 398 K	See Table 1	(24–27)
Linear thermal expansion coefficient	K^{-1}	D 696, 308–423 K	16-20 ($\times 10^{-5}$)	(28)
Solvents	—	368 K	Decalin, toluene	(29)
		369 K	Xylene	(29)
		371 K	Tetralin	(29)
		341 K	Cyclohexene	(30)
		374 K	*n*-Tetracosane	(30)
Nonsolvents	—	359 K	Methylene chloride	
		361 K	*o*-Dichloro benzene	
		366 K	1,2-Dichloropropane	
Mark-Houwink parameter: K and a	$K = ml\,g^{-1}$ $a =$ None	Decahydronaphthalene, 410 K	$K = 4.6 \times 10^{-4}$, $a = 0.73$	(31, 32)
		TCB, 408 K	$K = 3.63 \times 10^{-4}$, $a = 0.72$	(33)
Crystallographic data	Å	Unit cell dimensions depends on comonomer type and amount, and lamellae thickness	See Table 2	(13, 24, 34–36)
Degree of crystallinity	%	DSC (see also Table 3)	33–53	(3–6, 11, 24, 35, 37)
Heat of fusion	$kJ\,mol^{-1}$	DSC (see also Table 3)	1.37–2.18	(3–6, 11, 24, 35, 37)
Density, commercial resin	$g\,cm^{-3}$	D 1505-85	0.912–0.930	(10–12)
		D 792		(28)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Avarami exponent	–	Dependent on counit content and is independent of counit type; copolymer fractions of butene-1 4-MP-1 and octene-1 = 0.7–5.2 mol% range; isothermal crystallization range = 365–385 K	1.8–2.8	(4)
Long period spacing and lamellae thickness	Å	Raman longitudinal acoustic mode (LAM) and small-angle X-ray scattering (SAXS)	See Table 4	(5, 24, 35–37)
Surface free energy σ_e (chain-folding crystal face)	$J\,m^{-2}$	Dependent on counit content; counit content range = 0.70–7.6 mol%	0.067–0.225	(4, 38, 39)
Crystal phase structure	%	Raman LAM	See Table 3	(40)
Crystal orientation and birefringence	–	Wide-angle X-ray (WAXD) and infrared diachroism	See Table5	(41)
Radius of gyration $R_G/M^{0.5}$	$Amol^{0.5}g^{0.5}$	Hydrogenated polybutadiene, 18 ethyl/1,000 C, SANS	0.440	(42)
Melting temperature	K	DSC peak endotherms (dual endotherm, peak range)	378–383, and 394–398	(3-6, 11, 24, 35, 37)

Equilibrium melting point T_m [4, 37–39, 43, 44]

Copolymer	M_w	M_w/M_n	Counit (mol%)	Method	T_m^0 (K)	Reference
Butene-1	–	–	2.2	Thompson-Gibbs	406	(37, 38)
Butene-1	–	–	7.3	Thompson-Gibbs	407, 411	(37, 38)
Octene-1 (metallocene)	98400	2.2	1.5	Thompson-Gibbs	412.5	(44)
Octene-1 (metallocene)	102,700	2.1	3.6	Thompson-Gibbs	407.3	(44)

Note: The equilibrium melting temperature (T_m^0) of copolymers depends on the molecular weight, sequence distribution and counit content. The T_m^0 value is determined by two commonly used techniques: the Hoffman-Weeks plot and the Thompson-Gibbs plot. The application of the Hoffman-Weeks method to determine the T_m^0 of a copolymer is unreliable (see reference 43). The more reliable method is to use the Thompson-Gibbs relationship of T_m as a function of lamellar thickness, provided a large range of lamella thickness can be obtained. Considerable disagreement exists between different authors on the exact value of transition that can be identified for the copolymers. Consequently, values tabulated in this table must be used cautiously. See references (39, 43, and 44) for detailed discussions.

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Transition temperatures and activation energy*

Copolymer	Designation	Temperature range (K)	Activation energy (kJ mol^{-1})	Reference
Octene-1	α	333	62	(45)
(Dow 321)	β	253	319	(45)
tan δ peak at 10 Hz	γ	153	40	(45)
Octene-1	α	333	–	(46)
MI = 3.3, density = 0.912 g cm^{-3}	β	256	–	(46)
tan δ peak at 1 Hz	γ	150	–	(46)
Butene-1	α	304	–	(46)
MI = 1, density = 0.890 g cm^{-3}	β	253	–	(46)
tan δ peak at 1 Hz	γ	155	–	(46)

*Conditions: DMA.

Note: The transitions and relaxation temperatures associated with amorphous regions are designated as α, β, γ, etc. in descending temperature order. The values of T_α depends only on crystallite thickness. The temperature of beta transition, T_β, does not depend on the crystallite thickness but rather on the comonomer type and content. The γ transition is associated with glass transition. All transition values depend on the frequency of the DMA test. See reference (47) for a detailed discussion.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Vicant softening point	K	D1525	353–367	(28, 33)
Tensile modulus	MPa	D 638	137–520	(10–12, 28, 33)
Tensile yield strength	MPa	D 638	9–20	(10–12, 28, 33)
Elongation at break	%	D 638	100–1,200	(10–12, 28, 33)
Yield stress	MPa	D 638	6.2–11.5	(10–12, 33)
Flexural modulus	MPa	D 790, 298 K	235–800	(10–12, 28, 33)
Impact strength, notched Izod	J m^{-1}	D 256A	53.0–no break	(10, 28, 33)
Hardness	Shore D	D 676	47-58	(10, 28, 33)
Low temperature brittleness F_{50}	K	D 746	<197	(10–12, 33)
Blown film properties	–	See Tables 6 and 7	–	(11, 12, 16, 48, 50, 52)
Refractive index n_D^{25}	–	D 542	1.52	(10)
Dielectric constant	–	D 150	2.3	(28)
Loss factor, tan δ	–	D 150, up to 100 MHz (at 1 MHz)	<0.0005	(28)
Melt index	g $(10\ min)^{-1}$	D 1238	0.2–50	(11, 12)
Sonic velocity	m s^{-1}	MD and TD, blown films	See Table 5	(41)
Flow activation energy	kJ mol^{-1}	RMS, MI = 1.0, density = 0.918 gm cm^{-3}, temp. range = 423–483 K	30–32	(49)

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Table 1. Characteristic ^{13}C NMR bands by short-chain branching type[24, 25]

Chemical shift (ppm)		Chemical shift (ppm)		Chemical shift (ppm)		Chemical shift (ppm)	
Butene	Sequence assignment*	Hexene	Sequence assignment*	Octene	Sequence assignment*	4-MP-1	Carbon assignment*
40.2	BBBB	41.4	HHHH	40.33	OOOO	44.5	3-C
39.56	BBBE + EBBB	40.86	HHHE + EHHH	38.24	EOE	35.7	–CH–
37.24	EBB + BBE	40.18	EHHE	34.62	EOEE + EEOE	34.6	alpha-C
35.0	BBB	38.13	EHE	32.22	EOE	26.8	beta-C
34.5	EBEB + BEBE	35.85	EHH + HHE	30.47	OEEE + EEEO	25.8	2-C
34.33	EBEE + EEBB	35.0	HHEH + HEHH	27.27	EOE	23.0	3-C
30.92	BEEB	34.9	EHH + HHE	27.09	OOEE + EEOO		
30.47	BEEE + EEEB	34.54	EHEE + EEHE	22.89	EOE + EOO + OOE + OOO		
27.7	BBB	34.13	EHE	14.17	EOE + EOO + OOE + OOO		
27.27	EBEE + EEBE	30.94	HEEH				
27.1	BBEE + EEBB	30.47	HEEE + EEEH				
26.68	EBE	29.51	EHE				
11.2	EBE	29.34	EHH + HHE				
11.0	EBB + BBE	27.28	EHEE + EEHE				
10.81	BBB	27.09	HHEE + EEHH				
		24.39	EHEHH + HHEHE				
		24.25	HHEHH				
		23.37	EHE + EHH + HHE + HHH				
		14.12	EHE + EHH + HHE + HHH				

*E, B, H, and O refers to ethylene, butene, hexene, and octene comonomers. ^{13}C NMR assignment at 50.3 MHz in 10% 1,2,4-trichlorobenzene solution at 125°C. Internal standard = tetramethylsilane.

Table 2. Unit cell information*

Lattice	Space group	Comonomer		Unit cell dimensions (Å)			Reference
		Type	mol%	*a*	*b*	*c*	
Orthorhombic	Pnam	Butene	0.3	7.43	4.95	–	(34)
		Butene	0.6	7.45	4.95	–	(34)
		Butene	1.29	7.46	4.95	2.571	(36)
		Butene	3.85	7.48	4.97	2.571	(36)
		Butene	8.45	7.50	5.01	2.571	(36)
		Hexene	0.3	7.42	4.94	–	(34)
		Hexene	0.6	7.42	4.95	–	(34)
		Octene	0.065	7.429	4.950	–	(35)
		Octene	3.76	7.500	4.966	–	(35)
		Octene	5.0	7.571	4.987	–	(35)
		Octene	5.5	7.48	4.97	–	(34)

*Measured unit cell dimensions are dependent on lamellae thickness, which in turn depends on the crystallization temperature, comonomer type, and amount (see references 13 and 34–36 for details).

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Table 3. Physical properties of commercial grade LLDPEs as a function of counit content and type*[(40)]

Counit type	M_w ($\times 10^{-3}$)	Counit (mol%)	Crystallinity (%)	α_c (%)	α_a (%)	α_b (%)	Modulus (MPa)	Yield stress (MPa)	Ultimate tensile stress	Draw ratio at break
Butene	104	0.6	39	46	36	18	152	20.3	296	9.9
	105	1.88	22	30	52	18	106	12.3	195	6.8
Hexene	65	0.34	63	63	27	10	361	32.1	264	10.6
Octene	98	0.62	41	48	35	16	160	18.4	224	7.4
	99	0.90	37	43	42	15	144	16.2	219	7.0
	70	0.94	39	40	42	18	163	16.4	191	6.9
	103	1.33	35	35	47	18	123	13.2	197	6.4
	81	1.77	49	26	52	22	75	9.5	183	8.1
	128	2.58	12	14	67	19	35	5.9	93	7.0
	228	5.38	4	7	76	17	3	1.8	–	–

*Samples were compression molded and slow cooled in air; tensile properties were determined at a draw rate of 25.4 mm min^{-1}; percent crystallinity was determined by DSC at a heating rate of 10°C min^{-1}; crystal phase structures were determined by Raman internal mode technique (LAM); α_c, α_b, and α_a refer to fraction of chain units in the perfect crystals, interfacial region, and amorphous region, respectively of a lamella.

Table 4. Long-period spacings and lamellae thickness of LLDPE fractions by short-chain branching type*

Comonomer type	Mol% branching	M_w ($\times 10^{-4}$)	M_w/M_n	Conditions	Long-period spacing (Å)	Lamellae thickness (Å)	Reference
Butene-1	1.29	13.0	2.96	SAXS	162	75	(36)
	2.29	19.0	5.55		118	52	(36)
	3.17	9.93	3.09		105	55	(36)
	3.85	8.22	3.11		105	45	(36)
	5.10	4.61	2.90		92	50	(36)
	8.45	2.66	4.73		80	43	(36)
Butene-1	0.42	14.0	7.14	Raman LAM	–	91	(5)
	1.15	–	–		–	75	(5)
	3.43	–	–		–	72	(5)
	4.10	–	–		–	56	(5)
Hexene-1	1.57	259	11.5	Raman LAM	153	–	(24)
4-MP-1	1.76	94.5	5.0	Raman LAM	157	–	(24)
	2.74	91.2	4.0		130	–	(24)
	3.53	107.0	4.0		122	–	(24)
Octene-1	1.49	5.35	2.60	Raman LAM	–	80	(5)
	2.49	235.0	5.9		132	–	(24)
Octene-1	0.065	25.20	2.20	SAXS	369	163	(35)
	1.32	17.63	2.44		275	130	(35)
	2.22	14.62	2.75		187	70	(35)
	2.81	12.82	2.76		166	51	(35)
	3.76	9.40	2.86		140	43	(35)
	5.0	4.93	3.37		116	24	(35)

*Crystallization conditions are not known.

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Table 5. Morphological properties and crystal orientation of LLDPE (hexene-1) blown tubular films[41]

Thickness (μm)	Density ($g\,cm^{-3}$)	Birefringence ($\times 10^3$)	Sonic velocity ($km\,s^{-1}$)		Infrared diachroic ratio at 730 cm^{-1}	X-ray angle (degrees)			
						a-axis		*b*-axis	
			MD	TD	MD/TD	MD-TD	ND-MD	MD-TD	ND-MD
27.1	0.9116	−0.7478	828	1,009	1.26	90	90	0	0
24.7	–	+1.99	818	951	1.39	90	90	0	0
17.0	0.9172	0.00	843	717	1.24	90	90	0	0

Table 6. Physical properties of commercial grade LLDPE film samples as a function of comonomer type*

PROPERTY	UNITS	CONDITIONS	BUTENE	HEXENE	OCTENE
Melt index	g (10 min)$^{-1}$	D 1238	1.0	1.04	1.04
Density	$g\,cm^{-3}$	D 1505	0.919	0.919	0.920
Total SCB	CH_3/1,000 C	NMR	21.7	17.9	13.7
Peak melting point	K	DSC, 10°C min^{-1}, cooling and heating rates	372 and 395	372 and 397.5	371 and 394
Heat of fusion	$kJ\,mol^{-1}$	DSC, 10°C min^{-1}, cooling and heating rates	1.50	1.68	1.65
M_w ($\times 10^{-5}$)	$g\,mol^{-1}$	GPC, 408 K in TCB	1.3	1.24	1.36
M_w/M_n	–	GPC	3.7	4.1	4.6
Total haze	%	D 1003	15	16	12
Gloss, 45°D	Units	D 2457	46	41	48
Narrow angle scattering	%	D 1746	7	20	34
Modulus, 1% secant	MPa	D 882, MD D 882, TD	185 227	206 250	200 230
Dart impact (per mil)	g	D 1709, D 4272	74	187	201
Elmendorf tear	g	D 1922, MD D 1922, TD	58 520	270 710	340 750
Tensile strength at break	MPa	D 882, MD D 882, TD	41 18	39 20	58 31
Elongation at break	%	D 882, MD D 882, TD	430 560	430 550	440 600

*See references (11, 48, 50, and 51) for the effect of blowing conditions on film properties of LLDPEs. The result in this table was obtained for the following blown film conditions: blow-up ratio = 2.5 : 1; die gap = 2.54 mm; output = 32 kg h^{-1}; film thickness = 25.4 mm; die size = 102 mm; frost line height = 230 mm; melt temperature = 483 K.[52]

Table 7. Comparison of blown film properties of butene-1, 4-MP-1 copolymer, and butene/4-MP-1 terpolymer* (16)

PROPERTY	UNITS	CONDITIONS†	BUTENE COPOLYMER	BUTENE/4-MP-1 TERPOLYMER	4-MP-1 COPOLYMER
Modulus, 1% secant	MPa	D 882, MD	154	205	277
		D 882, TD	205	234	354
Dart drop, F-50 at 66 cm (per mil)	g	D 1709 and D 4272	140	161	180
Elmendorf tear (per mil)	g	D 1922, MD	200	240	250
		D 1922, TD	470	540	720
Tensile strength at break	MPa	D 882, MD	24.7	33.5	42
		D 882, TD	18.8	25.8	31.7
Tensile strength at yield	MPa	D 882, MD	7.9	10.7	12.7
		D 882, TD	8.75	11.7	13.5
Elongation at break	%	D 882, MD	460	460	510
		D 882, TD	620	600	680

*Approximate melt index of 1 g $(10\,\text{min})^{-1}$ and density 0.920 g cm^{-3}. Extrusion conditions: blow-up ratio = 2 : 1; die gap = 2.03 mm; output = 32 kg h^{-1}; film thickness = 31.75 μm; die size = 63.5 mm; frost line height = unknown; melt temperature = 466 K.
†MD and TD referes to machine and transverse directions film properties.
Note: The film properties of Tables 6 and 7 should not be compared due to different extrusion conditions.

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Polyethylene, low-density

A. PRASAD

ACRONYMS LDPE, branched PE, high-pressure PE

CLASS Poly(α-olefin)

STRUCTURE $-[CH_2-CH_2]_n-$

INTRODUCTION LDPE is produced under high pressure (82–276 MPa) and high temperature (405–605 K) with a free radical initiator (such as peroxides and oxygen) and contains some long chain branches (LCB), which could be as long as chain backbones,[1,2] and short chain branches (SCB).[3] It is produced by either a tubular or a stirred autoclave reactor.[4] The autoclave process can produce LDPE resins having a wide range of molecular weight distribution (MWD) and less LCB in comparison with a tubular reactor. [4] Long chain branching has a strong influence on MWD, and hence on resin properties, such as processibility, melt strength, and film optical properties. [4] SCBs disrupt chain packing and are principally responsible for lowering the melting temperature and the crystal density for hydrocarbon polymers. LDPE is commercially available in a wide variety of molecular weight, MWD, SCB, and LCB contents, and density ranges.[4–6]

Thermal and mechanical properties of semicrystalline polymers are strongly dependent on MW, MWD, branching content, and density.[5,7,8] Controlled variations in these structural parameters result in a broad family of products with wide differences in thermal and mechanical properties. Shear modified LDPE samples are also available commercially.[9,10] The deliberate shearing of polymer melt results in a reduction in melt viscosity and elasticity without significant change in MW.[11] These reversible changes are advantageous for molding and extrusion and also result in film with better optical properties.[9,10,12] Shear modified LDPEs show vastly different crystallization rates.[12] The properties shown in the following table are given in ranges because of their dependence on molecular structure and are intended to represent best published examples of most commonly used commercial grades of LDPE for blown film, molding, and extrusion coating applications. Table 3 contains properties of tubular blown films.

MAJOR APPLICATIONS Major applications include blown film for bags and packaging; extrusion coatings for paper, metal, and glass; and injection molding for can lids, toys, and pails. Other applications include blow molding (squeeze bottles), rotomolding and wire and cable coatings, carpet backing, and foam for packaging material. There is considerable use of blends of LDPE with high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) in a wide variety of applications. These blends are deliberately excluded in the data presented below.

PROPERTIES OF SPECIAL INTEREST LDPE has a good balance of mechanical and optical properties with easy processibility and low cost. It can be fabricated by many different methods for a broad range of applications. Special properties of interest include: optical clarity, flexibility, toughness, high impact strength, good heat seal, low brittleness temperature, good chemical resistance to aqueous solvents, and good electrical properties. LDPE may not be suitable for applications that require

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high stiffness and high tensile strength. Other limitations include: poor resistance to oxidizing agents, aliphatic solvents, aromatic solvents, polar liquids, chlorinated solvents, low softening point, poor scratch resistance, poor gas and moisture permeability, and relatively lower stress-crack resistance when compared to other types of polyethylene. LDPE undergoes thermal degradation at high temperatures and chain extension under shear conditions.

MAJOR SUPPLIERS Equistar Chemicals LP., Dow Chemical Co., Chevron Chemical Co., Westlake Plastics Co., Du Pont Co., Exxon Chemical Co., Eastman Chemical Co., Union Carbide Corp., Mobil Polymers, Rexene Corp., Novacor Chemicals, Inc.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Type of branching	—	FTIR, NMR	Methyl, ethyl, butyl, amyl and longer branches	(13–15)
Type of unsaturation	%	FTIR		(16)
		Vinylidene	80	
		Vinyl	10	
		Trans	10	
Degree of SCB, commercial grades	Methyl/1,000 carbon	FTIR, NMR	10-33	(13-15)
Typical M_w range, commercial grades	g mol^{-1}	GPC	$3–40 \times 10^4$	(5, 16)
Typical polydispersity index (Mw/Mn)	—	GPC, strongly influenced by the amount of LCB	4–30	(17–19)
IR (characteristic absorption frequencies)	cm^{-1}	Thin film sample at room temperature	See table below	(14, 15, 20)

Characteristic frequencies of crystalline LDPE*

Wave number	Intensity	Assignments
720	Very strong	CH_2 rocking
731	Very strong	CH_2 rocking
888	Very weak	Vinylidene groups
890	Very weak	CH_3 rocking
908	Medium	Terminal vinyl groups
964	Very weak	*Trans* double bond
990	Weak	Terminal vinyl groups
1,050	Very weak	CH_2 twisting
1,176	Very weak	CH_2 wagging
1,375	Weak-medium	CH_3 symmetrical bending
1,457	Very weak	CH_3 asymmetrical bending
1,463	Very strong	CH_2 bending

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Characteristic frequencies of crystalline LDPE*

Wave number	Intensity	Assignments
1,473	Very strong	CH_2 bending
2,850	Very strong	CH_2 symmetrical stretching
2,857	Very strong	CH_2 symmetrical stretching
2,874	Weak	CH_3 symmetrical stretching
2,899	Very strong	CH_2 asymmetrical stretching
2,924	Very strong	CH_2 asymmetrical stretching
2,960	Weak	CH_3 asymmetrical stretching

*Observed in the infrared spectra and band assignments.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Linear thermal expansion coefficient	K^{-1} ($\times 10^{-5}$)	D 696 Temperature range = 238–423 K	10.0–51.0 See table below	(21–23) (5, 16)

Temp. (K)	Coefficient of expansion ($\times 10^{-5}$)	
	Linear	Cubical
238	10.0	30.0
273	18.3	55.0
293	23.7	71.0
313	29.0	87.0
333	33.7	101.0
353	40.3	121.0
373	46.6	140.0
383	51.0	153.0
388–423	25.0	75.0

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density (amorphous)	$g\,cm^{-3}$	At 298 K, extrapolated from melt temperature	0.855	(24, 25)
Solvents	–	368 K 369 K 371 K 341 K 374 K	Decalin, toluene Xylene Tetralin Cyclohexene *n*-Tetracosane	(26, 27)
Nonsolvents	–	359 K 361 K 366 K	Methylene chloride *o*-Dichloro benzene 1,2-Dichloropropane	(27)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Solubility parameter	$(MPa)^{1/2}$	*n*-Tetracosane, 374 K	15.20	(27)
		Cyclohexene, 341 K	17.10	(27)
		n-Heptane, 359 K	14.57	(27)
		n-Octane, 361 K	14.50	(27)
		n-Hexane, 359 K	12.46	(27)
		n-Pentane, 361 K	12.52	(27)
		Chloroform, 350 K	16.00	(27)
		Carbon tetrachloride, 346 K	14.77	(27)
		Tetrachloroethylene, 346 K	15.69	(27)
		Chlorobenzene, 349 K	18.13	(27)
		o-Dichlorobenzene, 361 K	18.62	(27)
		Methylene chloride, 359 K	13.75	(27)
		See also the other references for more data	—	(27, 28–31)
Theta temperature θ	K	Bis(2-ethylhexyl)adipate	418–443	(28)
		Bis(2-ethylhexyl)sebacate	423	
Flory interaction parameter χ	—	*n*-Tetracosane, 374 K	−0.09	(27)
		Cyclohexene, 341 K	−0.03	(27)
		n-Heptane, 359 K	0.13	(27)
		n-Octane, 361 K	0.18	(27)
		n-Octane, 393 K	0.31	(29)
		n-Octane, 418 K	0.30	(29)
		n-Hexane, 359 K	0.23	(27)
		n-Pentane, 361 K	0.35	(27)
		Toluene, 393 K	0.34	(29)
		Xylene, 350 K	0.51	(29)
		m-Xylene, 393 K	0.29	(29)
		p-Xylene, 393 K	0.27	(29)
		Chloroform, 350 K	0.25	(27)
		Tetrachloroethylene, 346 K	-0.05	(27)
		Chlorobenzene, 349 K	0.04	(27)
		o-Dichlorobenzene, 361 K	0.41	(27)
		Methylene chloride, 359 K	0.60	(27)
		Carbon tetrachloride, 346 K	0.01	(27)
		See also the other references for more data	—	(27–29)
Second virial coefficient A_2	$mol\,cm^3\,g^{-2}$	Tetralin, 334 K		(32, 33)
		$M_w = 5.73 \times 10^5$	0.92×10^{-4}	
		$M_w = 1.98 \times 10^6$	0.84×10^{-4}	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Mark-Houwink parameters: K and a	$K = \text{ml g}^{-1}$ a = None	Should be used for approximate MW values only because LDPE contains long-chain branching	—	(32–36)
		Decalin, 342 K	$K = 3.87 \times 10^{-4}$, $a = 0.78$	(36)
		p-Xylene, 347 K	$K = 1.05 \times 10^{-3}$, $a = 0.63$	(33)
		Xylene, 353 K	$K = 1.35 \times 10^{-4}$, $a = 0.63$	(34)
Characteristics ratio $\langle r^2 \rangle / nl^2$	—	Tetralin, 334 K	7.26, 7.58	(32)
Crystallographic data	Å	Wide-angle X-ray (WAXD)	See table below	(37–40)

Unit cell information

Lattice	Space group	Unit cell dimensions (Å)			Monomers per unit cell	Reference
		a	*b*	*c*		
Orthorhombic	Pnam	7.40	4.93	2.534	2	(37)
		7.36	4.92	—	—	(38)
		7.51	4.97	—	—	(39)
Monoclinic	C2/m	8.09	2.53	4.79	2	(40)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Crystallinity	%	DSC	33–53	(41–48)
Heat of fusion (per repeat unit)	kJ mol^{-1}	DSC	1.37–2.18	(41–48)
Density	g cm^{-3}	Commercial resins, ASTM D 1505	0.910–0.935	(4–6)
		Unit cell, 100% crystalline	1.00	(37)
		Unit cell, 100% crystalline	1.014	(38)
Lamellae thickness	Å	Raman longitudinal acoustic mode (LAM), various crystallization conditions used	See Table 1	(16, 48)
Crystal phase structure	%	LAM	See Table 1	(48)
Crystal orientation and birefringence	—	WAXD and infrared diachroism	See Table 2	(58)
Melting temperature	K	DSC, peak endotherms	378–388	(5, 6, 41, 44)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature	K	DMA, TMA	140–170 (See also transition and relaxation temperature table below)	(45–47)
Transition and relaxation temperatures; and activation energy*	—	DMA	See table below	(16, 45–49)

*The transitions and relaxation temperatures associated with amorphous regions are designated as α, β, γ, etc. in descending temperature order. Several conflicting interpretations and values have been given regarding the origin and molecular nature of the transitions in LDPE (see references 45 to 49). It is believed that the values of T_a depends on crystallite thickness. The temperature of beta transition, T_β, does not depend on the crystallite thickness but rather the comonomer type and content. The γ transition is associated with glass transition. All transition values depend on the frequency of the DMA test. See references (46) and (47) for detailed discussions. The transition temperatures associated with peaks in dynamic loss listed in this table are given in ranges because of a wide range of values cited in the literature (for a specific examples see Table 1 below).

Transitions	Temperature range (K)	Approximate activation energy (kJ mol^{-1})
α	293–360	>420
β	233–280	160–200
γ	140–170	32–75

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat capacity (of repeat units)	kJ k^{-1} mol^{-1}	At constant pressure and temperature of 298 K, (density = 0.921 g cm^{-3})	1.6536×10^{-4}	(50, 51)
		At other temperatures	—	(51)
Enthalpy (of repeat unit)	kJ mol^{-1}	Calorimeter		(51)
		Temperature (K)		
		80	0.287	
		140	0.883	
		200	1.722	
		260	2.887	
		320	4.545	
		380	7.619	
		415	9.384	
Entropy (of repeat unit)	kJ k^{-1} mol^{-1}	Calorimeter		(51)
		Temperature (K)		
		80	0.00586	
		140	0.0114	
		200	0.0164	
		260	0.0214	
		320	0.0273	
		380	0.0357	
		415	0.0406	

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Polyethylene, low-density

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Deflection temperature	K	D 648, at 273 K and 0.45 MPa	311–322	(23)
Heat distortion temperature	K	D 648, 455 KPa	313–323	(21)
Vicant softening point	K	D 1525	363–375	(5)
Tensile modulus	MPa	D 638	102–310	(5, 21, 52)
Compressive strength	MPa	D 695	18–25	(23)
Tensile yield strength	MPa	D 638	9–15	(5, 21, 52)
Elongation at break	%	D 638	100–800	(5, 21, 52)
Yield stress	MPa	D 638	6.2–11.5	(5, 21, 52)
Flexural modulus	MPa	D 790 at 298 K	240–330	(6, 21, 52)
Impact strength, notched Izod	$J\,m^{-1}$	D 256A	No break	(6, 21, 52)
Hardness	Shore D	D 676	40–60	(5, 6, 21, 52)
Low-temperature brittleness F_{50}	K	D 746	<197	(21, 52)
Refractive index	–	D 542, crystalline (value depends on density and chain branching)	1.5168–1.5260	(21, 53)
		Amorphous	1.49	(16, 54)
		Refractive index in melt	See table below	(54)
Specific volume	$cm^3\,g^{-1}$	Differential refractometer and dilatometer, Alathon 10	See table below	(54)
Specific refractivity	$cm^3\,g^{-1}$	Differential refractometer and dilatometer, Alathon 10	See table below	(54)

Temperature (K)	Specific volume ($cm^3\,g^{-1}$)	Refractive index	Refractivity ($cm^3\,g^{-1}$)
363.16	1.159	1.4801	0.3293
368.16	1.168	1.4736	0.3281
373.16	1.178	1.4693	0.3283
378.16	1.195	1.4630	0.3291
381.16	1.209	1.4575	0.3297
384.16	1.282	1.4510	0.3290
386.16	1.239	1.4432	0.3286
391.16	1.250	1.4392	0.3289
387.56	1.256	1.4368	0.3288

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric constant ε'	—	D 150 at 1 kHz		(5, 21, 55)
		Density ($g\,cm^{-3}$)		
		0.920	2.28	
		0.930	2.30	
		0.935	2.31	
Loss factor, tan δ	—	Up to 100 MHz	10^{-4}–10^{-3}	(5, 21)
Dielectric strength	$Mv\,cm^{-1}$	D 149, 283 K	7.0	(21, 55, 56)
		D 149, 373 K	2.0	
Power factor	—	D 150 at 1 kHz	0.0003	(5)
Melt index	$g\,(10\,min)^{-1}$	D 1238	0.2–50	(4, 6)
Flow activation energy: EH and E_V*	$kJ\,mol^{-1}$	RMS, melt index = ~1 g $(10\,min)^{-1}$ density = 0.919–0.931 $g\,cm^{-3}$, temp. range = 423–483 K	E_H = 61–67 E_V = 8–10.5	(59)
Coefficient of sliding friction μ	—	D 1894, dynamic c.o.f. to stainless steel, melt index = 2 g $(10\,min)^{-1}$ density = 0.915 $g\,cm^{-3}$	0.7	(57)
Sonic velocity	$m\,s^{-1}$	Blown films	See Table 2	(58)
Water absorption	%	D 570, 24 h	<0.02	(21)

*The horizontal shift factor reflects the temperature dependence of relaxation time, and the vertical shift factor reflects the temperature dependence of modulus.

Table 1. Morphological and relaxation properties of LDPE as a function of crystallization condition* (48)

Condition	α-Relaxation (K, 3.5 Hz)	β-Relaxation (K, 3.5 Hz)	Crystallinity (%)	Crystallite thickness (Å)	% Crystal phase structure		
					α_c	α_a	α_b
Slow cooled	348	258	36	105	37	49	14
Cooled in air	323	258	—	82	—	—	—
Quenched 80°C	323	258	40	80	36	53	11
Quenched 40°C	278	—	—	70	—	—	—
Quenched 0°C	273	—	32	—	—	—	—
Quenched −120°C	270	—	29	65	38	49	13

*$M_w = 3.46 \times 10^5$, M_w/M_n = 18.5, total SCB/1,000 C = 10.6, LCB/1,000 C = 2.2.
Note: Compression molded specimens were rapidly quenched to the specified quenching temperatures. Relaxation temperatures (tan δ peaks) were obtained on a DMA instrument at a heating scan rate of 1°C min^{-1}. Crystal phase structures were obtained by Raman LAM. The degree of crystallinity was determined from the heat of fusion data obtained on a DSC instrument.

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Table 2. Morphological properties and crystal orientation of LDPE (density 0.920 $g\,cm^{-3}$) blown tubular films[58]

Thickness (μm)	Density ($g\,cm^{-3}$)	Birefringence ($\times 10^3$)	Sonic velocity ($m\,s^{-1}$)		Infrared diachroic ratio (at 730 cm^{-1})	X-ray angle (degree)			
						a-axis		*b*-axis	
			MD*	TD*	MD/TD*	MD-TD*	ND-MD*	MD-TD*	ND-MD*
54	0.9182	–9.79	953	1,128	1.15	45–50	45–60	0	0
26	–	–8.23	870	1,003	0.88	45	45–60	0	0
23	0.9175	–3.07	852	998	1.13	70	60–70	0	0

*MD, TD, and ND refers to the machine, transverse, and normal direction of a blown film sample.

Table 3. Blown film properties of high clarity grade LDPE*

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melt index	$g\,(10\,min)^{-1}$	D 1238	2.0	(66)
Density	$g\,cm^{-3}$	D 1505	0.924	(66)
Peak melting point	K	DSC, 10°C min^{-1} cooling and heating rate	382.5	(66)
Heat of fusion	$kJ\,mol^{-1}$	DSC, 10°C min^{-1} cooling and heating rate	1.50	(66)
M_w	$g\,mol^{-1}$	GPC, 408 K in 1,2,4-trichlorobenzene	79,200	(66)
M_w/M_n	–	GPC	3.8	(66)
Total haze	%	D 1003	5.2	(66)
Gloss, 45°D	Units	D 2457	71	(66)
Narrow angle scattering	%	D 1746	72	(66)
Modulus, 1% secant	MPa	D 882, MD D 882, TD	200 240	(66)
Dart impact (per mil)	g	D 1709, D 4272	74	(66)
Elmendorf tear	g	D 1922, MD D 1922, TD	360 220	(65)
Tensile strength at break	MPa	D 882, MD D 882, TD	25 17	(66)
Elongation at break	%	D 882, MD D 882, TD	290 500	(66)

*Film and optics properties depend upon processing conditions (see references 9, 10, 60–65). This table presents some representative values of typical high clarity grade LDPE films processed using the following conditions: blow-up ratio = 2 : 1; die gap = 0.635 mm; output = 48 $kg\,h^{-1}$; film thickness = 30.5 μm; die = 203 mm; frost line height = 330 mm; melt temperature = 463 K.

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Polyethylene, metallocene linear low-density

A. PRASAD

ACRONYMS, ALTERNATIVE NAMES mLLDPE, metallocene PE, single site catalyzed LLDPE (SSC), polyolefin plastomers (POP), homogeneous ethylene copolymers

CLASS Poly(α-olefins)

STRUCTURE $-[CH_2{-}CH_2{-}CHR{-}CH_2]_n-$ (R = α-olefin)

INTRODUCTION New types of linear low-density polyethylenes (LLDPE) based on the metallocene catalyst technology have been introduced recently in the market place. Metallocene-based Ziegler-Natta catalysts utilize a new synthetic approach for the polymerization of poly(α-olefins).[1–5] Metallocene precatalysts are based primarily on group IV transition metals (primarily titanium and zirconium straddled by a pair of cyclic alkyl molecules) and require a coactivator, which is typically methylalumoxane but certain acids containing noncoordinating anions as bases also work well.

This new family of polyolefin copolymers has a significantly different chain microstructure than conventional LLDPE.[6–15] The single site characteristics of metallocenes, with the catalyst site being identical, are known to produce materials having the most probable molecular weight distribution ($M_w/M_n \sim 2.0$), with essentially a random comonomer distribution and narrow composition distribution. The comonomers most frequently used commercially are butene, hexene, and octene. Copolymerization of ethylene with 4-methyl-1-penetene (4-MP-1) and cyclic and bicylic groups has been also reported in the literature.[16] Several terpolymers are also commercially available.[11] Exxon Chemical Company manufactures ethylene-butene copolymers, ethylene-hexene copolymers, and terpolymers of butene and hexene comonomers. Exxon markets these mLLDPEs under the trademark name of Exxpol™ Exact PE (density range of 0.910–0.865 g cm^{-3}) and Exxpol™ Exceed PE (density range of 0.925–0.910 g cm^{-3}). Dow Chemical Company manufactures ethylene-octene copolymers using constrained geometry catalyst technology (CGCT™). The Dow mLLDPE trade mark names are Engage™, Affinity™ and Enhanced™ PE. The Affinity resins range in density from 0.902 to 0.935 g cm^{-3}, in weight percent comonomer from 2 to 12% octene comonomer, and melt index (MI) from 1.0 to 3.5 g $(10\,min)^{-1}$.

Metallocene LLDPEs are relatively difficult to process because of narrow molecular weight distribution (MWD) when compared to conventional Ziegler LLDPEs.[10] Metallocene catalyst based octene-1 LLDPE copolymers made by the Dow Chemical Company are known to process better as a result of their long-chain branched (LCB) structure, referred to as Dow Rheology Index (DRI) numbers.[10, 17] The LCB is also responsible for improved melt strength in mLLDPEs.[13] Exxon has also addressed the processibility issue with advanced performance terpolymers.[11] LCB bimodal mLLDPE resins are commercially available from BP Chemicals.[18] Such mLLDPEs are produced by BP's proprietary gas phase fluid bed technology called Innovene™ technology.[18]

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Besides molecular weight (MW) and molecular weight distribution (MWD), mechanical and thermal properties of LLDPE depend on the comonomer amount (density), composition distribution, and comonomer type.[5, 6, 8, 13, 15, 19–21] The comonomer type is also referred to as short-chain branches (SCB). Consequently, mLLDPEs have quite different mechanical properties than conventional LLDPE made by Ziegler-Natta type catalyst. The mLLDPEs are commercially available in wide variety of MI and density ranges. The materials in the density range of 0.885 0.863 g cm^{-3} are called elastomeric PE and are presented in the entry on *Polyethylene, elastomeric (very highly branched)*, in this handbook. Metallocene LLDPEs of density greater than 0.886 g cm^{-3} are called plastomers. This entry covers properties of mLLDPE plastomers in the density range of 0.886 to 0.935 g cm^{-3}. Due to wide range of MI and density, mLLDPE properties shown in the following table are given in ranges. Here, only those properties are listed that differ substantially from the conventional Ziegler-Natta type LLDPE and are intended to represent best published examples of commercially available grades of mLLDPE resins. The physical properties of extruded materials may vary substantially from those of the compression molded samples. For illustration purposes, some of the compression molded samples and blown film properties that depend on the chemical nature of the comonomer are listed in Tables 2, 3, and 4.

MAJOR APPLICATIONS Major applications include blown and cast packaging films, injection molding goods, medical devices, automotive applications, wire and cable coatings, electrical cables, adhesives, and sealants. Other applications include blow molding, pipe and conduit, rotomolding, foams for sporting goods and houseware goods.

PROPERTIES OF SPECIAL INTEREST Flexibility, low extractability, high shock resistance, high toughness, exceptionally high dart-impact strength and puncture resistance, balanced machine and transverse direction tear strength, better clarity, low heat seal temperature, better electrical/abrasion properties, good organoleptic properties and better biaxial orientation than conventional LLDPEs. Other properties of interest include low brittleness temperature, good chemical resistance to acids and aqueous solvents, good heat seal, good stress-crack resistance properties, and good structural stability at high temperatures.

LIMITATIONS mLLDPEs without the long-chain branching are relatively difficult to process because of narrower MWD. Other limitations include: poor stretchability, no significant advantage in film tear properties, and higher resin cost when compared to conventional Ziegler LLDPE.

MAJOR SUPPLIERS Dow Chemical Co., Exxon Chemical Co., BP Chemicals, BASF, Mitsubishi Chemical Corp., Mitsui Petrochemicals, Mobil Polymers.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Typical comonomer	—	Butene, hexene, octene	—	(1, 5, 6–8)
Degree of branching, commercial resins	mol%	NMR, ethyl, butyl, and hexyl branches	0.5–7.0	(3,15)
Typical molecular weight range (M_w)	g mol^{-1}	GPC, in 1,2,4-trichlorobenzene	4–11 ($\times 10^4$)	(22)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Typical polydispersity index (M_w/M_n)	—	GPC	2–2.5	(5, 17, 19)
Crystallographic data*	Å	Wide angle X-ray	See table below	(23)

*Crystalline unit cell parameters depend on crystallite thickness. The comonomer amount, comonomer type, and crystallization conditions determine the crystallite thickness in ethylene copolymers. The major cause of lattice expansion in ethylene copolymers is due to decrease in lamellae thickness by exclusion of branch points from the lamellar crystals coupled with surface stress on thin lamellae (see references 24 and 25 for details). The table below is for butene-1 mLLDPE ($M_w = 122{,}000$, $M_w/M_n = 2$), crystallized from the melt at a cooling rate of $7^\circ C\,min^{-1}$.

Lattice	Mol%	Unit cell dimensions (Å)			Unit cell volume (nm^3)	Unit cell density ($g\,cm^{-3}$)
		a	*b*	*c*		
Orthorhombic	3.0	7.53	5.00	2.54	0.0959	0.9724
	5.2	5.58	4.99	2.54	0.0963	0.9679

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Crystallinity	%	DSC	33–53	(5–9, 19)
Heat of fusion	$kJ\,mol^{-1}$	DSC	1.37–2.18	(5–9, 19)
Density, commercial resins	$g\,cm^{-3}$	D1505-85	0.886–0.940	(15, 26)
Avrami exponent*	—	Depends on counit content and crystallization temperature	See table below	(27, 28)

*A caution should be exercised in using Avrami exponent values for the copolymers. In contrast to homopolymer crystallization, the isotherms of copolymers do not superpose one with the other; deviations from the Avrami relation occurs at low levels of crystallinity; and retardation in crystallization rate is pronounced with the extent of transformation due to continuous change in both composition and sequence distribution during crystallization. See reference (28) for the detailed discussion. Avrami exponent values for selected mLLDPE are shown below.

Comonomer	Mole (%)	Crystallization condition	Value	Reference
Octene	<7.5	Not known	2–4	(27)
Octene	>7.5	Isotherm crystallization: <328 K	2	(27)
Octene	>7.5	Isotherm crystallization: >328 K	1	(27)
Hexene	1.21	Isotherm crystallization: 381–388 K	3	(28)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Lamellae thickness and crystal phase structure	Å and %	Raman longitudinal acoustic mode (LAM), small-angle X-ray (SAXS), transmission electron microscopy (TEM)	See Table 1	(14, 19, 20, 23)
Surface free energy, σ_e (chain-folding crystal face)	$J\,m^{-2}$	Thomson-Gibbs equation; value is dependent on counit content:		
		Octene-1 0.9 mol%	0.066	(20)
		Octene-1 3.9 mol%	0.096	(20)
		Octene-1 2.4 mol%	0.214–0.286	(29)
		Octene-1 4.7 mol%	0.268–0.357	(29)
		Butene-1 7.5 mol%	0.268–0.357	(29)
Melting temperature T_m	K	DSC peak endotherm, density range = 0.886–0.935 $gm\,cm^{-3}$ (T_m depends on MW and SCB content but not on SCB type. Single and multiple endotherms have been observed)	363–398	(5–9)
Transition and relaxation temperatures	K	DMA tan δ peaks at 1 Hz, heating rate = 3°C min^{-1} (values depend on mol% branching); value for 2.8–8.2 mol%, octene-1	α = 322–373 β = 245–232 γ = 153–163	(8, 30, 31)
Vicant softening point	K	D 1525, density range = 0.920–0.912 $gm\,cm^{-3}$	382–368	(12, 32)
Tensile modulus	MPa	D 412, <1% strain, density range = 0.887–0.935 $gm\,cm^{-3}$	20–550	(15)
		2–3% strain, independent of comonomer type, depends on crystallinity, value for crystallinity range of 7–50%	4–70	(19)
		D 1708, octene-1		(8)
		Density = 0.916 $gm\,cm^{-3}$	400	
		Density = 0.9014 $gm\,cm^{-3}$	120	
		ISO 527, octene-1		(32)
		298 K, density = 0.909 $gm\,cm^{-3}$	200	
		Density = 0.935 $gm\,cm^{-3}$	700	
Elongation at break	%	D 638	>700, no break	(33)

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Yield stress*[8, 19, 32, 34]

Comonomer	Mole (%)	$M_w \times 10^4$ (g cm^{-3})	Density (%)	Crystallinity	Conditions	Yield stress (MPa)	Reference
Butene	0.95	5.3	–	40.0	Specimen quenched to 195 K, draw rate = 2.54 cm min^{-1}	12.0	(19)
	1.26	9.0	–	37.0		10.4	(19)
	2.05	12.5	–	27.0		8.3	(19)
Hexene	0.6	5.6	–	40.0	Same as above	11.4	(19)
	1.1	5.8	–	36.0		10.3	(19)
	2.8	5.7	–	19.0		5.6	(19)
	3.5	6.3	–	15.0		5.5	(19)
4-MP-1	0.7	12.7	–	37.0	Same as above	10.0	(19)
	1.3	13.7	–	27.0		7.0	(19)
	2.0	10.6	–	26.0		7.0	(19)
	2.1	23.8	–	18.0		3.5	(19)
Octene	0.7	11.7	–	40.0	Same as above	12.0	(19)
	1.4	7.9	–	28.0		7.5	(19)
	4.6	14.9	–	7.0		2.1	(19)
	0.005	8.25	0.935	–	ISO 527	20.0	(32)
	1.8	9.67	0.909	–	ISO 427	8.0	(32)
	2.8	–	0.9209	46.0	D 1708	13.0	(8)
	5.2	–	0.9029	33.0	D 1708	7.8	(8)

*Yield stress value is independent of comonomer type but depends on crystallinity value.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Flexural modulus	MPa	ISO 178, octene-1		(32)
		298 K, density = 0.909 gm cm^{-3}	125	
		Density = 0.935 gm cm^{-3}	635	
Ultimate tensile stress	MPa	Depends on MW and counit content, has maximum value at $\sim M_w$ of 10^5 for all the copolymers; for $M_w = 10^5$		(19)
		mol% branch =< 1	48	(19)
		mol% branch = 1–3.5	38	(19)
		mol% branch => 3.5	32	(19)
		mol% octene = 2.8	34.6	(8)
		mol% octene = 5.2	30.9	(8)
Impact strength, notched Izod	J m^{-1}	ISO 180, octene-1		(32)
		298 K, density = 0.909 gm cm^{-3}	No break	
		Density = 0.935 gm cm^{-3}	2,500	
Dynatup impact	J	D 3763-86, several mLLDPE used		(35)
		Butene-1: density = 0.912 gm cm^{-3}	17	
		Butene-1: density = 0.921 gm cm^{-3}	13	
		Octene-1: density = 0.912 gm cm^{-3}	27	
		Octene-1: density = 0.921 gm cm^{-3}	19.5	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Hardness	Shore A	D 2240, octene-1, 6.2 mol%	75	(36)
Volume resistivity	ohm cm ($\times 10^{14}$)	1 mm thick sample		(37)
		Density = 0.915 g cm^{-3}		
		293 K	10,800	
		313 K	2,220	
		333 K	54.0	
		363 K	1	
		Density = 0.935 cm^{-3}		
		293 K	32,000	
		313 K	10,000	
		333 K	550	
		363 K	18.0	
Melt index	g (10 min)$^{-1}$	D 1238	0.8–30	(26)
Water vapor transmission rate (WVTR)	g m^{-2} day^{-1}	Test temperature = 311 K; relative humidity = 90%; butene-1: density range = 0.900–0.910 g cm^{-3}	15.5–19.5	(38)
Oxygen transmission rate (OTR)	mmol cm/ cm^2 h kPa	Test temperature = 273–298 K; various types of mLLDPE	6–10 ($\times 10^{-8}$)	(38, 39)
Carbon dioxide transmission rate (CO_2TR)	mmol cm/ cm^2 h kPa	Test temperature = 273–298 K; various types of mLLDPE	8–50 ($\times 10^{-8}$)	(38, 39)

Table 1. Crystal phase structure and lamellae thickness of mLLDPE by short chain branching type*

Comonomer	Mole % branch	M_w ($\times 10^{-4}$)	Conditions†	Lamellae thickness (Å)	% Crystallinity (DSC)	α_a (%)	α_b(%)	α_c(%)	Reference
Butene	0.95	5.3	A	87	34	44	16	40	(19)
	1.26	9.0		93	31	46	17	37	(19)
	2.05	12.5		72	24	62	11	27	(19)
Butene	3.0	12.2	B	47	33	45	10	45	(23)
	5.2	11.9		29	25	47	15	38	(23)
Hexene	0.6	5.6	A	95	41	48	12	40	(19)
	1.1	5.8		82	35	46	18	36	(19)
	1.2	10.4		77	–	58	10	32	(19)
	2.2	8.8		62	–	68	12	20	(19)
	3.5	6.27		57	12	67	18	15	(19)
Hexene	1.9	9.65	C	86	49	9	41	50	(14)
			D	71	–	13	42	45	(14)

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Table 1. (*continued*)

Comonomer	Mole % branch	M_w ($\times 10^{-4}$)	Conditions†	Lamellae thickness (Å)	% Crystallinity (DSC)	α_a (%)	α_b(%)	α_c(%)	Reference
4-MP-1	0.7	12.7	A	72	40	55	8	37	(19)
	1.3	13.7		67	38	61	12	27	(19)
	2.0	10.6		–	28	55	19	26	(19)
	3.6	6.3		50	19	67	22	11	(19)
Octene	0.7	11.7	A	87	34	47	13	40	(19)
	1.4	7.9		78	27	52	20	28	(19)
	4.6	14.9		45	8	82	11	7	(19)
Octene	0.9	7.7	E	140	60	–	–	–	(20)
	3.9	8.14		72	41	–	–	–	(20)

*α_c, α_b, and α_a refers to fraction of chain units in the perfect crystals, interfacial region, and amorphous region, respectively of a lamella. See references (7) and (19) for more data and detailed discussions.
†A = LAM, quenched to 195 K. B = SAXS, sample cooled at 7°C min^{-1}. C = Lamella thickness by TEM, crystal phase structure by ^{13}C NMR; samples were crystallized isothermally at 383 K for 18 h. D = quench cooled to 73 K. E = SAXS, sample cooled at 20°C min^{-1}.

Table 2. Blown film properties comparison of ethylene-octene mLLDPEs of different densities and conventional Ziegler ethylene-octene LLDPE*

PROPERTY	UNITS	CONDITIONS	MLLDPE1 (OCTENE)	MLLDPE2 (OCTENE)	MLLDPE3 (OCTENE)	LLDPE (OCTENE)
Melt index	g (10 min)$^{-1}$	D 1238	0.85	1.5	1.6	1.0
Density	g cm^{-3}	D 1505	0.920	0.912	0.895	0.920
Total short-chain branch	Mol%	NMR	1.7	2.4	3.7	2.7
M_w/M_n	–	GPC	2.0	2.0	2.0	4.6
Total haze	%	D1003	12	11	1.1	11.3
Gloss, 45°D	Units	D2457	61	63	90	61
Modulus, 2% secant	MPa	D882, MD	206	152	53	190
		D882, TD	230	152	55	215
Dart impact	g	D1709, D4272	>850 (no break)	650	>850 (no break)	266
Elmendorf tear	g	D1922, MD	740	1,190	550	980
		D1922, TD	990	1220	590	1,210

*The results in Table 2 were obtained for the following blown film conditions: blow-up ratio = 2.5 : 1; die gap = 1.78 mm; output not mentioned; film thickness = 50.5 mm; die size = 152.4 mm; frost line height not mentioned; melt temperature = 508 K.[12,40]

Note: It is well-known that film properties depend on the chemical nature of the comonomer.[41–43] However, blown film properties also depend on the processing conditions.[41,43–45] Properties listed in Tables 2 and 3 were obtained at different extrusion conditions and, therefore, should not be compared.

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Table 3. Blown film properties comparison of ethylene-hexene mLLDPEs of different densities and conventional Ziegler ethylene-hexene LLDPE*

PROPERTY	UNITS	CONDITIONS	MLLDPE (HEXENE)	MLLDPE (HEXENE)	MLLDPE (HEXENE)	LLDPE (HEXENE)
Melt index	$g\ (10\ min)^{-1}$	D 1238	0.80	1.0	1.0	1.04
Density	$g\ cm^{-3}$	D 1505	0.925	0.918	0.917	0.919
Total short-chain branch	Mol%	NMR	2.18	3.38	3.66	3.88
Peak melting point	K	DSC, at a cooling and heating rate of $5°C\ min^{-1}$	385 and 394	379.5 and 392.5	379.5 and 391.5	372 and 397.5
Heat of fusion	$kJ\ mol^{-1}$	DSC, at a cooling and heating rate of $5°C\ min^{-1}$	1.93	1.49	1.49	1.68
$M_w \times 10^{-5}$	$g\ mol^{-1}$	GPC, 408 K in 1,2,4-trichlorobenzene	1.37	1.22	1.25	1.24
M_w/M_n	–	GPC	2.7	2.4	2.6	4.1
Total haze	%	D1003	19	12	10	16
Gloss, 45°D	Units	D2457	38	58	61	41
Modulus, 1% secant	MPa	D882, MD D882, TD	305 290	187 185	175 168	206 250
Dart impact	g	D1709, D4272	230	860	1040	215
Elmendorf tear	g	D1922, MD D1922, TD	300 450	230 480	260 420	360 710
Tensile yield	MPa	D 882, MD D 882, TD	11.8 14.0	9.0 8.7	8.9 11.1	9.6 11.2
Elongation at yield	%	D 882, MD D 882, TD	6 16	8 12	8.5 20	8 14
Tensile strength break	MPa	D 882, MD D 882, TD	56 57	61 49	58 47	35 22
Elongation break	%	D 882, MD D 882, TD	530 650	580 600	560 580	420 540
Hexene extractables	%	312 K for 2 h	<1	<1	<1	>3

*The results in Table 3 were obtained for the following blown film conditions: blow-up ratio = 2.5 : 1; die gap = 2.54 mm; output = $30\ kg\ h^{-1}$; film thickness = 28 mm; die size = 102 mm; frost line height = 330 mm; melt temperature = 475 K.[46] See also references (5, 11, 13, 35, 47) for more data.

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Table 4. Blown film properties comparison of ethylene-octene and ethylene-butene mLLDPEs of different densities with the compression molded specimens*

PROPERTY	UNITS	CONDITIONS	BUTENE-1	OCTENE-1	BUTENE-1	OCTENE-1
Melt index	$g\,(10\,min)^{-1}$	D 1238	0.94	0.93	0.97	1.02
Density	$g\,cm^{-3}$	D 792	0.912	0.912	0.921	0.921
Total short-chain branch	Mol%	NMR	4.17	3.04	3.04	1.77
Peak melting point	K	DSC, at a cooling and heating rate of $10^{\circ}C\,min^{-1}$	374.2	379.4	383.3	386.5
M_w ($\times 10^{-4}$)	$g\,mol^{-1}$	GPC, 423 K in 1,2,4-trichlorobenzene	7.54	9.0	7.28	8.3
M_w/M_n	–	GPC	2.22	2.12	2.25	2.19
COMPRESSION MOLDED SAMPLE PROPERTIES						
Intrinsic tear	g	Elmendorf A tear test using 254 μm sample (normalized to per mil)	86	345	63	300
Dynatup impact	J	D 3763-86	17.0	27.0	13.0	19.5
Tensile yield	MPa	D 638	8.68	8.96	12.00	11.64
Tensile break	MPa	D 638	15.73	25.61	14.63	24.14
Tensile strain at break	%	D 638	743	697	640	767
BLOWN FILM SAMPLE PROPERTIES						
Density (film)	$g\,cm^{-3}$	D792	0.9086	0.9085	0.9177	0.9173
Film haze	%	D1003	5.01	3.92	6.86	5.33
Dart impact	g	D1709	184	>860	50	188
Elmendorf tear	g	D1922, MD	85	237	26	208
		D1922, TD	475	475	163	392
Tensile yield	MPa	D 882, MD	6.2	6.4	11.8	12.4
		D 882, TD	5.6	6.2	11.9	12.9
Tensile strength at break	MPa	D 882, MD	29.1	53.8	28.2	57.0
		D 882, TD	20	51.0	22.1	45.5
Elongation at break	%	D 882, M D	586	622	497	571
		D 882, TD	651	744	567	629

*The results in Table 4 were obtained for the following blown film conditions: blow-up ratio = 2.5 : 1; die gap = 1.78 mm; output = 14.5 $kg\,h^{-1}$; film thickness = 25.4 mm; die size = 76.2 mm; frost line height = 28 cm; melt temperature unknown.[35]

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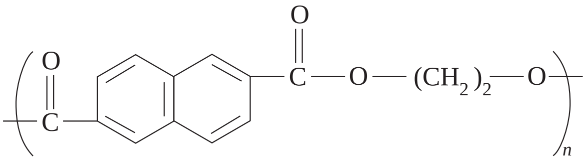
Poly(ethylene-2,6-naphthalate)

JUDE O. IROH

ACRONYM PEN

CLASS Polyesters; linear aromatic rigid polyesters; thermoplastics

STRUCTURE



MAJOR APPLICATIONS Films, rigid thermoplastic polyesters.

PROPERTIES OF SPECIAL INTEREST Mostly synthesized as semicrystalline thermoplastic. PEN is a clear and rigid polyester.

PREPARATIVE TECHNIQUES Synthesized by step-growth polymerization of ethylene glycol and naphthalene-2,6-dicarboxylate.[1]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular conformation	—	—	Nearly planar	—
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	242	—
Glass transition temperature T_g	K	DSC	390–394	(2–4, 8)
Melting temperature T_m	K	DSC	538–539	(2–4, 8)
Crystallization temperature	K	DSC	471–476	(2, 3)
Heat of fussion ΔH	$kJ\,mol^{-1}$	DSC 100% crystallinity	9.2 46	(2, 3)
Heat of cold crystallization ΔH_{cc}	$kJ\,mol^{-1}$	DSC	7.3	(2, 3)
Coefficient of thermal expansion α	K^{-1}	—	4.4×10^{-5}	(2)
Inherent viscosity	$dl\,g^{-1}$	Dilute solution viscometry	0.51–0.53	(2, 4)
Intrinsic viscosity	$dl\,g^{-1}$	Dilute solution viscometry at 25°C	0.59	(8)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Solvent	—	—	Phenol/*o*-dichlorobenzene	(7, 8)
Physical state	—	Semicrystalline	—	—
Unit cell	—	—	Triclinic	—
Lattice constants	—	X-ray diffraction	$a = 6.57$ $b = 5.75$ $c = 13.2$ $\alpha = 81°20'$ $\beta = 144°$ $\gamma = 100°$	(3, 5, 6)
Number of chains per unit cell	—	— X-ray diffraction	1 —	(5, 6)
Number of chains	—	—	1	(5, 6)
No of monomers	—	—	1	(5, 6)
Breaking strength σ_B	MPa	Tensile	83	(7)
Tensile (Young's) modulus E	MPa	—	2,000	(7)
Flexural strength σ^*	MPa	3-point flexure	108	(7)
Flexural modulus E	MPa	3-point flexure	2,500	(7)
Elongation ε_B	%	Tensile	48.53	(7)
Measured density	$g\,cm^{-3}$	Autodensimeter	1.3471	(7)

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Poly(ethylene oxide)

QINGWEN WENDY YUAN

ACRONYM PEO

CLASS Polyethers

STRUCTURE $[-CH_2-CH_2-O-]$

MAJOR APPLICATIONS Textile applications, cosmetics, antifoaming agents, others (chemical intermediates, ink and dye solvents, demulsifiers, plasticizers, etc.)[1,2]

PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–		44	–
Polymerization	–	–		Anionic ring-opening	(1)
Solvents	Benzene, alcohols, chloroform, esters, cyclohexanone, N,N-dimethylacetamide, acetonitrile, water (cold), aqueous K_2SO_4 (0.45 M above 35°C), aqueous $MgSO_4$ (0.39 M above 45°C)				(3)
Nonsolvents	Ethers, dioxane (sw), water (hot), aliphatic hydrocarbons				(3)
Theta temperature	K	Solvent*	Method†		
		Acetonitrile/*i*-propyl ether (45/55)	CP	293.5	(3, 4)
		Benzene/isooctane (100/48)	CT	344.3	(3, 5)
			PE	344.5	(3, 5)
		$CaCl_2$/water ($2\,mol\,l^{-1}$)	CT	355.5	(3, 6)
				359.5	(3, 7)
		Chloroform/*n*-hexane (54/46)	CT	293.5	(3, 8)
		Chloroform/*n*-hexane (47.4/52.6)	CT, VM	293.5	(3, 9)
		CsCl/water ($2\,mol\,l^{-1}$)	CT	333.5	(3, 6)
		Diethylene glycol diethylether	VM	323.5	(3, 10)
		KCl/water ($2\,mol\,l^{-1}$)	CT	327.5	(3, 7)
				330.5	(3, 6)
		KNO_3/water ($2\,mol\,l^{-1}$)	CT	338.5	(3, 7)
		K_2SO_4/water ($0.45\,mol\,l^{-1}$)	CT	307.5	(3, 11)
				307.5	(3, 7)
			PE	308.5	(3, 12)
			VM	308.5	(3, 10)
		LiCl/water ($2\,mol\,l^{-1}$)	CT	363.5	(3, 6, 7)
		Methyl *i*-butyl ketone	VM	323.5	(3, 10)
		$MgCl_2$/water ($2\,mol\,l^{-1}$)	CT	353.5	(3, 6)
				363.5	(3, 7)
		$MgSO_4$/water ($0.39\,mol\,l^{-1}$)	CT	315.5	(3, 11)
			CP	315.5	(3, 7)
			PE	318.5	(3, 12)

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Theta temperature	K	Solvent*		Method†		
		NaCl/water (2 mol l^{-1})		CT	333.5	(3, 6)
					334.5	(3, 7)
		NH_4Cl/water (2 mol l^{-1})		CT	349.5	(3, 6)
					350.5	(3, 7)
		Nitroethane/*i*-propyl ether (45/55)		CP	293.5	(3, 8)
		RbCl/water (2 mol l^{-1})		CT	329.5	(3, 6)
		$SrCl_2$/water (2 mol l^{-1})		CT	346.5	(3, 6)
					355.5	(3, 7)
		Water		DM, VM	278.6	(3, 13)
				CT	369.5	(3, 7)
					390.5	(3, 6)
Interaction parameter χ	—	Method: vapor pressure				
		Benzene, $T = 323.8$ K				
		$v_2 = 0.2$			0.18	
		$v_2 = 0.4$			0.14	
		$v_2 = 0.6$			0.10	
		Benzene, $T = 343.5$ K				
		$v_2 = 0.2$			0.19	
		$v_2 = 0.4$			0.14	
		$v_2 = 0.6$			0.12	
		$v_2 = 0.8$			0.09	
Second virial coefficient	mol cm^3 g^{-2} ($\times 10^{-4}$)	Solvent	Temp. (°C)	Mol. wt. (g mol^{-1})		
		Benzene	25	7.70×10^3	27.4	(3, 15)
			25	3.79×10^3	78	(3, 15)
		Dimethylformamide	—	3.79×10^3	30	(3, 15)
			25–120	$\sim 3.5 \times 10^3$	37–47	16)
		Methanol	25	7.70×10^3	66.0	(3, 15)
				3.79×10^3	56.0	(3, 15)
				$(0.316–6.75) \times 10^3$	18.0–16.4	(3, 17)
					170–34.8	(3, 18)
				$(0.062–37.3) \times 10^3$	1,220–46	(3, 18)
				$(1–31) \times 10^3$	102.5–39	(3, 19)
				$(1–10) \times 10^3$	84.5–47.5	(3, 20)
				$(4–23) \times 10^3$	87–46	(3, 21)
				$(3–48) \times 10^3$	48–27.5	(3, 22)
		Water	25	$(10.9–800) \times 10^3$	116–30.4	(3, 23)
				10.1×10^3	62	(3, 21)

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PROPERTY	UNITS	CONDITIONS			VALUE		REFERENCE
Huggins coefficient	–	Solvent	Temp. (°C)	$[\eta]$			(3)
		Benzene	20	2	~3.7		
				48	0.4		
		Chloroform	20	3	~0.9		
				82	0.4		
		Dimethylformamide	20	3	~0.6		
				45	0.4		
		Toluene	30	3	~2.50		
				39	0.4		
			35	1.1	8.16		
				1.9	3.41		
				2.4	2.06		
				5.5	2.3		
		Water	20	3	1.1		
				5	0.4		
			35	1.7	4.95		
				3.0	2.42		
				5.0	0.93		
				10.8	0.44		

PROPERTY	UNITS	Solvent	Temp. (°C)	Mol. wt. ($g\,mol^{-1}$)	K ($\times 10^{-3}$)	a	REFERENCE
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None	Acetone	25	$(7–100) \times 10^4$	32	0.67	(3, 11)
				$(0.02–0.3) \times 10^4$	156	0.50	(3, 24)
		Benzene	20	$(0.01–1.9) \times 10^4$	48	0.68	(3, 20)
			25	$(8–520) \times 10^4$	30.7	0.686	(3, 25)
				$(0.02–0.8) \times 10^4$	129	0.5	(3, 24)
		Carbon tetrachloride	20	$(0.02–1.1) \times 10^4$	69	0.61	(3, 20)
			25	$(7–100) \times 10^4$	62	0.64	(3, 11)
		Chloroform	25	$(0.02–0.15) \times 10^4$	206	0.50	(3, 24)
		Cyclohexane	20	$(0.006–1.1) \times 10^4$	$[\eta] = 0.5 + 0.035M^{0.64}$		(3, 20)
		Diethylene glycol diethyl ether	50	$(7–100) \times 10^4$	140	0.51	(3, 11)
		Dimethylformamide	25	$(0.1–3) \times 10^4$	$[\eta] = 2.0 + 0.024M^{0.73}$		(3, 19)
		Dioxane	20	$(0.006–1.1) \times 10^4$	$[\eta] = 0.75 + 0.035M^{0.71}$		(3, 20)
			25	$(0.02–0.15) \times 10^4$	138	0.5	(3, 24)
		Methanol	20	$(0.06–1.9) \times 10^4$	$[\eta] = 2.0 + 0.033M^{0.72}$		(3, 20)
			25	–	82.5	0.57	(3, 26)
		4-Methylpenta-2-one	50	$(7–100) \times 10^4$	120	0.52	(3, 11)
		Toluene	35	$(0.04–0.4) \times 10^4$	14.5	0.70	(3, 27)
		Water	20	$(0.006–1.1) \times 10^4$	$[\eta] = 2.0 + 0.016M^{0.76}$		(3, 26)
			25	$(0.019–0.1) \times 10^4$	156	0.50	(3)
			30	$(2–500) \times 10^4$	12.5	0.78	(3, 28)
			35	$(3–700) \times 10^4$	6.4	0.82	(3, 12)
				$(0.04–0.4) \times 10^4$	16.6	0.82	(3, 27)
			45	$(3–700) \times 10^4$	6.9	0.81	(3, 12)

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PROPERTY	UNITS	CONDITIONS			VALUE		REFERENCE
Mark-Houwink parameters: K and a	$K = \text{ml g}^{-1}$ a = None	Solvent	Temp. (°C)	Mol. wt. (g mol^{-1})	K ($\times 10^{-3}$)	a	
		Aqueous K_2SO_4 (0.45 M)	35	$(3\text{–}700) \times 10^4$	130	0.50	(3, 12)
				$(7\text{–}100) \times 10^4$	280	0.45	(3, 11)
		Aqueous $MgSO_4$ (0.39 M)	45	$(3\text{–}700) \times 10^4$	100	0.50	(3, 12)
Solubility parameter	$(\text{MPa})^{1/2}$	Method: IPGC, 25°C			20.2 ± 2		(3, 29)
Heat of solution	J g^{-1}	Semicrystalline polymer					(3)
		Benzene, 30°C, $4.3 \times 10^4 \text{ g mol}^{-1}$			170		
		Chloroform, 30°C, $6 \times 10^3 \text{ g mol}^{-1}$			52		
		Water, 25°C, $2 \times 10^4 \text{ g mol}^{-1}$			10		
		Water, 30°C, $6 \times 10^3 \text{ g mol}^{-1}$			24		
		Water, 30°C, $4.3 \times 10^4 \text{ g mol}^{-1}$			40		
Heat of fusion	kJ mol^{-1}	—			8.29		(3)
					9.5		
					8.04		
					11.7		
					9.41		
					7.86		
					8.7		
					7.33		
Glass transition temperature	K	Conflicting data; value ranges from 158 to 233 K			232(?)		(1, 30–37)
		Method: differential microcalorimeter; $R[(CH_2)_2O)]_n(CH_2)_2R$					(38)
		R = OH					
		$n = 1$			162.5		
		$n = 2$			170.5		
		$n = 3$			174.5		
		$n = 4$			176.5		
		$n = 5$			181.5		
		$n = 7$			183.5		
		R = Cl					
		$n = 1$			139.5		
		$n = 2$			157.5		
		$n = 3$			168.5		
		$n = 4$			177.5		
		$n = 5$			185.5		
		$n = 7$			187.5		
		Electron spin resonance			213		(39)
		Highly crystalline			206.5		(40)

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Melting temperature	K	Method: differential microcalorimeter; $R[(CH_2)_2O)]_n(CH_2)_2R$			(38)
		R = OH			
		$n = 1$	265.5		
		$n = 3$	262.5		
		$n = 4$	273.5		
		$n = 5$	282.5		
		$n = 7$	285.5		
		R = Cl			
		$n = 1$	209.5		
		$n = 3$	261.5		
		$n = 4$	254.5		
		$n = 5$	258.5		
		$n = 7$	249.5		
		Highly crystalline	339.5		(40)
Heat capacity C_p	$kJ\,K^{-1}\,mol^{-1}$ $(\times 10^{-3})$	Temp. (K)	Solid	Melt	(3, 41, 42)
		10	0.51	–	
		20	3.18	–	
		30	7.24	–	
		40	11.16	–	
		50	14.62	–	
		60	17.60	–	
		70	20.13	–	
		80	22.33	–	
		90	24.90	–	
		100	26.93	–	
		110	28.78	–	
		120	30.44	–	
		130	32.10	–	
		140	33.57	–	
		150	35.05	–	
		160	36.53	–	
		170	37.80	–	
		180	39.11	–	
		190	40.40	–	
		200	41.88	–	
		210	43.17	81.88	
		220	44.64	82.55	
		230	45.91	83.21	
		240	47.26	83.88	
		250	48.61	84.55	
		260	49.96	85.22	
		270	51.31	85.89	
		280	52.66	86.55	
		290	54.01	87.22	
		300	55.36	87.89	
		310	56.71	88.56	

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Heat capacity C_p	$kJ\,K^{-1}\,mol^{-1}$ ($\times 10^{-3}$)	Temp. (K)	Solid	Melt	(3, 41, 42)
		320	58.06	89.23	
		330	59.41	89.89	
		340	60.76	90.56	
		350	–	91.23	
		360	–	91.90	
		370	–	92.57	
		380	–	93.23	
		390	–	93.90	
		400	–	94.57	
		410	–	95.24	
		420	–	95.91	
		430	–	96.57	
		440	–	97.24	
		450	–	97.91	
Index of refraction	–	–	1.4563		(1)
		High molecular weight	1.51–1.54		

PROPERTY	UNITS	Solvent	Temp. (°C)	Mol. wt. ($g\,mol^{-1}$)	$\lambda_0 = 436\,nm$	$\lambda_0 = 546\,nm$	REFERENCE
Specific refractive index increment dn/dc	$ml\,g^{-1}$	Acetonitrile	25	62	0.0964	–	(3, 18)
				100	–	0.106	(3, 18)
				161	–	0.114	(3, 18)
				205	–	0.121	(3, 18)
				316	–	0.123	(3, 18)
				407	–	0.130	(3, 18)
				970	–	0.135	(3, 18)
				9,400	–	0.135	(3, 18)
		Benzene	–	106	−0.086	–	(3, 43)
			–	194	−0.073	–	(3, 43)
			–	282	−0.066	–	(3, 43)
			–	810	−0.059	–	(3, 43)
			25	3,510	–	−0.016	(3, 18)
			30	3,510	−0.018	–	(3, 44)
			54	3,510	−0.013	–	(3, 44)
			25	(0.15–53) $\times 10^4$	−0.017 to −0.010	–	(3, 45)
		Bromoform	23	–	−0.108	−0.090	(3, 46)
		n-Butanol	–	–	–	0.076	(3, 47)
		Carbon tetrachloride/methanol	25	–			
		(75/25 vol.)			–	0.066	(3, 48)
		(50/50 vol.)			–	0.091	(3, 48)
		(20/80 vol.)			–	0.128	(3, 48)
		Chlorobenzene	23	–	−0.039	−0.030	(3, 46)

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PROPERTY	UNITS	CONDITIONS			VALUE		REFERENCE
Specific refractive index increment *dn/dc*	ml g^{-1}	Solvent	Temp. (°C)	Mol. wt. ($g\,mol^{-1}$)	$\lambda_0 = 436\,nm$	$\lambda_0 = 546\,nm$	
		Chloroform	23	—	0.054	0.053	(3, 46)
			30	—	0.054	—	(3, 44)
		Chloroform/ *n*-hexane (47/53 vol.)	20	—	—	0.091	(3, 9)
		1,2-Dibromoethane	23	—	−0.048	−0.044	(3, 46)
		Dioxane	—	10,000	—	0.045	(3, 43)
			45	—	0.061	—	(3, 44)
		Methyl ethyl ketone	—	810	—	0.092	(3, 43)
			—	10,000	—	0.094	(3, 43)
		Methanol	—	—	—	0.150	(3, 47)
			25	62	—	0.118	(3, 20)
				100	—	0.127	(3, 18)
				161	—	0.135	(3, 18)
				205	—	0.139	(3, 18)
				316	—	0.141	(3, 18)
				445	—	0.142	(3, 18)
				810	—	0.143	(3, 43)
				1,020	—	0.144	(3, 18)
				3,000	—	0.149	(3, 43)
				6,000	—	0.150	(3, 43)
				9,400	—	0.150	(3, 18)
				10,000	—	0.148	(3, 43)
				31,000	—	0.150	(3, 18)
			25	—	0.143	—	(3, 9)
			45	—	0.152	—	(3)
			30	—	0.145	0.142	(3)
			45	—	0.150	—	(3, 44)
		Methyl acetate	25	6,700	—	0.111	(3, 18)
		Pyridine	23	6,700	−0.026	-0.018	(3, 46)
		1,1,2,2-Tetrachloroethane	23	6,700	0.006	0.007	(3, 46)
		Tetrahydrofuran	—	6,700	—	0.068	(3, 47)
		Water	27	6,700	0.134	0.132	(3, 49)
					—	0.139	(3, 47)
			20	6,700	0.138	0.135	(3, 49)
			25	—	0.138	—	(3, 49)
			30	—	0.136	—	(3, 49)
			40	—	0.134	0.132	(3, 49)
			50	—	0.133	0.131	(3, 49)
			25	62	0.093	—	(3, 43)
				106	0.108	—	(3, 43)
				194	0.124	—	(3, 43)
				300	0.126	0.123	(3, 43)
				600	0.135	0.131	(3, 43)
				810	0.136	0.128	(3, 43)

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PROPERTY	UNITS	CONDITIONS			VALUE			REFERENCE
Specific refractive index increment dn/dc	ml g^{-1}	Solvent	Temp. (°C)	Mol. wt. ($g\,mol^{-1}$)	$\lambda_0 = 436\,nm$	$\lambda_0 = 546\,nm$		
		Water		1,200	0.139	0.134		(3, 43)
				3,000	0.141	—		(3, 43)
				6,000	0.145	0.139		(3, 43)
				9,400	—	0.135		
				10,000	0.142	—		(3, 43)
				14,400	—	0.139		(3, 50)
			80	14,400	—	0.115		(3, 50)
				31,000	—	0.135		(3, 18)
				340,000	0.149	—		(3, 51)

PROPERTY	UNITS	Solvent	Mol. wt. ($g\,mol^{-1}$)	20°C	150°C	200°C	REFERENCE
Surface tension	$mN\,m^{-1}$	Diol	86–17,000	42.9	30.1	25.2	(3, 52–54)
			6,000	42.9	33.0	29.2	
			6,000	42.5	30.1	25.4	
		Dimethylether	114	28.6	16.0	11.1	
			148	31.1	18.6	13.8	
			182	32.9	20.5	15.8	
			600	37.5	26.1	21.7	
			5,000	44.1	32.7	28.3	
			100,000	44.2	32.8	28.4	

PROPERTY	UNITS	Solvent	Temp. (°C)	Mol. wt. ($g\,mol^{-1}$)	VALUE	REFERENCE
Diffusion coefficient	$cm^2\,s^{-1}$ ($\times 10^{-7}$)					(3)
		Acetone	25	4.3×10^3	37.8	
		Formamide	25	4.3×10^3	5.76	
		Methanol	25	4.3×10^3	23.5	
				23.8×10^3	10.7	
				19.2×10^3	10.7	
		Water	20	0.29×10^3	37.0	
				0.625×10^3	29.2	
				1.25×10^3	24.0	
				3.3×10^3	13.3	
				5.8×10^3	11.6	
				8.8×10^3	10.3	
				10.6×10^3	7.2	
				1.426×10^3	23.6	
				1.470×10^3	22.6	
				1.778×10^3	19.7	
				1.822×10^3	20.1	
			25	4.3×10^3	11.5	
				238×10^3	4.85	
				12×10^3	7.35	
				23.8×10^3	4.85	
				37.3×10^3	3.95	
				17.7×10^3	1.33	

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Diffusion coefficient	$cm^2\ s^{-1}$ ($\times 10^{-7}$)	Solvent	Temp. (°C)	Mol. wt. ($g\ mol^{-1}$)		(3)
		Water	25	30.0×10^3	1.08	
				67.9×10^3	0.79	
				119×10^3	0.63	
				$1,130 \times 10^3$	1.33	
				$1,470 \times 10^3$	1.36	
				$1,900 \times 10^3$	1.15	
				$2,000 \times 10^3$	1.12	
				$2,610 \times 10^3$	0.93	
				$2,630 \times 10^3$	0.93	
				$2,670 \times 10^3$	0.94	
				320×10^3	1.0	
Dipole moment per momomer unit	D	Solvent	Temp. (°C)	P_n		(3)
		Dioxane	25	1–7	1.68–1.29	
		Benzene	20	1.0–33.6	1.41–1.09	
		Benzene	20	2–227	1.46–1.07	
		Benzene	25	4.1–153.0	1.61–1.13	
		Benzene	25	4.0–176.2	1.68–1.13	
		(End group: $-OC_2H_5$)				
		Benzene	20	2 and 6	1.15 and 1.11	
		Benzene	25	1–6	1.14–1.07	
		Benzene	50	1–6	1.14–1.09	

*Numbers in parenthesis are compositions in volume/volume.
†CP = cloud point; CT = cloud temperature; VM = intrinsic viscosity/molar mass; PE = phase equilibria; DM = diffusion coefficient/molar mass.

Crystalline-state properties[3]

Lattice	Space group	Unit cell parameters (Å)			Angles (degrees)	Monomers per unit cell	Density ($g\ cm^{-3}$)
		a	*b*	*c*			
Monoclinic	—	9.5	19.5	12.0	$\beta = 101$	36	1.207
Monoclinic	C2H-5	8.05	13.04	19.48	$\beta = 125.4$	28	1.229
Monoclinic	CS-2	8.03	13.09	19.52	$\beta = 125.1$	28	1.220
Monoclinic	—	7.95	13.11	19.39	$\beta = 124.6$	28	1.231
Monoclinic	—	8.02	13.4	19.25	$\beta = 126.9$	28	1.238
Monoclinic	—	8.16	12.99	19.30	$\beta = 126.1$	28	1.239
Monoclinic	—	7.51	13.35	19.90	$\beta = 118.6$	28	1.169
Triclinic	CI-1	4.71	4.44	7.12	$\alpha = 62.8$, $\beta = 93.2$, $\gamma = 111.4$	2	1.197

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Poly(ethylene sulfide)

JUNZO MASAMOTO

ACRONYM PES

CLASS Polysulfides

STRUCTURE $-(S-CH_2CH_2)-$

MAJOR APPLICATION Poly(ethylene sulfide) is a high melting plastics material. However, this polymer has not yet achieved commercial production, although its properties makes it warrant serious consideration as a plastic.[1]

PROPERTIES OF SPECIAL INTEREST Poly(ethylene sulfide) is a high melting crystalline material. High-molecular-weight polymers prepared by ring-opening polymerization of ethylene sulfide have melting points generally above 478 K. The melting point of PES is much higher compared to poly(ethylene oxide) (melting point = 341 K). Only a few solvents are known that dissolve PES, but only at temperatures above 413 K. PES requires addition of stabilizers to permit processing in standard molding equipment, the best of which are polyamines with high boiling points and their derivatives. The polymer, properly stabilized, can best be molded using screw injection-molding equipment at temperature of 488–523 K.[2]

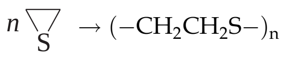
PREPARATIVE TECHNIQUES There are two different pathways (polycondensation and ring-opening polymerization) for preparation of PES.[2] The first method leads to a polymer of relatively low molecular weight, whereas the ring-opening polymerization reaction can lead to high molecular weight polymers under particular circumstances.

Following is the polycondensation reaction:[3,4]

$$Br-CH_2CH_2-Br + nK_2S \rightarrow (-C_2H_4S-)_n + 2nKBr$$

Condensation of an ethylene dihalide with an alkali metal sulfide[3] was studied in the latter part of the nineteenth century. The acid catalyzed polycondensation of certain mercapto alcohols represents a second method of synthesis.[4]

Following is the ring-opening polymerization reaction:[2,5]



It was found by Thiokol Chemical Corp. (Trenton, New Jersey, USA) that a catalyst formed by the reaction of diethyl zinc with water readily produces ethylene sulfide polymers that melted at 481–485 K.[5]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	60	–
Typical molecular weight range of polymer	$g\,mol^{-1}$	Determined from zero-intercept melt viscosity	$1.4–8 \times 10^5$	(6, 7)
IR (characteristic absorption frequencies)	cm^{-1}	Rocking motion CH_2 Stretching C–S Twisting CH_2 Wagging CH_2 Symmetric deformation CH_2	672 724 1,183 1,259 1,427	(8)
Solvents	A few solvents are known that dissolve PES at temperature above 140°C		α-methylnaphthalene, nitorobenzene, *o*-dichlorobenzene, dithiolane, dimethyl sulfoxide	(2)
Nonsolvents	No ordinary solvent is known that dissolve PES at temperatures below 140°C			(2)
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ $a =$ None	Solvent: dithiolane and stabilizer, at 160°C	$K = 2.2 \times 10^{-3}$ $a = 0.65$	(9)
Melt viscosity-molecular weight	–	M = molecular weight; G = melt index ($g\,min^{-1}$)	$\log M = 5.14 - 0.4167(\log G)$	(7)
Characteristic ratio $\langle r^2 \rangle / nl^2$	–	–	4.2	(10, 11)
Lattice	–	–	Orthorhombic	(12–14)
Space group	–	–	Pbcn-D2h-6	(12–14)
Chain conformation	–	–	CH_2–CH_2 *trans* CH_2–S Gauche (right-handed) S–CH_2 Gauche (right-handed) CH_2–CH_2 trans CH_2–S Gauche (left-handed) S–CH_2 Gauche (left-handed)	(8, 12, 15, 16)
Crystalline state conformation	–	–	(2/0) glide plane	(12)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Unit cell dimensions		X-ray photograph of oriented sample	$a = 8.50$, $b = 4.95$, $c = 6.70$ (fiber axis)	(12)
		Electron diffraction of single crystal and fiber	$a = 8.508$, $b = 4.938$, $c = 6.686$ (fiber axis)	(13, 14)
Unit cell contents	–	–	4 monomeric units per unit cell (2 molecular chains)	(12)
Degree of crystallinity	%	X-ray diffraction and density	50–68	(9)
Heat of fusion	$kJ\,mol^{-1}$	100% crystallinity	$H_0 = 14.1$	(9)
	$J\,g^{-1}$	54% crystallinity sample	126	
Entropy of fusion	$J\,K^{-1}\,mol^{-1}$	–	$S_0 = 28.8$	(9)
Density	$g\ cm^{-1}$	Theoretical density for crystalline PES	1.41	(12)
		Observed density	1.33–1.34	(12)
		Amorphous density	1.295	(9)
Glass transition temperature	K	Extraporation from the $T_g$values of amorphous copolymers ethylene sulfide/isobutylene sulfide. DSC, heating rate = $10^{\circ}C\,min^{-1}$	223	(17)
Melting point	K	–	481–485	(2)
			489	(11, 19)
Deflection temperature	K	1.8 MPa	432	(2)
Tensile modulus	MPa	–	2,200	(2)
		At 20°C	1,800	(9)
		At 70°C	1,060–1,150	(9)
		At 125°C	770–790	(9)
		Unaged	2,070	(1)
		Aged 7 days at 120°C	2,200	(1)
		Aged 7 days at 150°C	2,500	(1)
Tensile strength	MPa	–	72	(2)
		At 20°C	70–78	(9)
		At 60°C	56–62	(9)
		At 100°C	38–48	(9)
		At 125°C	30–38	(9)
		Unaged	68	(1)
		Aged 7 days at 120°C	39	(1)
		Aged 7 days at 150°C	32	(1)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Maximum extensibility (elongation)	%	–	10	(2)
		At 20°C	10–14	(9)
		At 60°C	12	(9)
		At 100°C	25–40	(9)
		At 125°C	40–50	(9)
		Unaged	15	(1)
		Aged 7 days at 120°C	4.2	(1)
		Aged 7 days at 150°C	3.7	(1)
Flexural modulus	Mpa	–	2,070	(1)
Flexural strength	MPa	–	72	(1)
Notched Izod impact strength	$J\,m^{-1}$	–	69	(2)
		Unaged	64	(1)
		Aged 7 days at 120°C	16	(1)
		Aged 7 days at 150°C	16	(1)
Melt viscosity	Pa s	Theoretical molecular weight		(9)
		80,000	4,950	
		9,500	570	
Melt index	$g\,min^{-1}$	235°C	0.01–0.2	(6)
Pyrolyzability, nature of product	Without stabilizer, above the melting point (225°C), the polymer viscosity falls rapidly with pronounced darkening and the liberation of volitiles		Ethylene, hydrogen sulfide, dithiane, methyldithiolane	(1, 6)
Pyrolyzability, amount of product	mol gas (unit ES)$^{-1}$ min^{-1}	223°C, N_2	6.0×10^{-5}	–
		230°C, N_2	8.7×10^{-5}	
		240°C, N_2	39.4×10^{-5}	
		250°C, N_2	76.1×10^{-5}	
Pyrolyzability, amount of impurities	Stability is influenced by the nature of initiator. Polymers initiated by zinc or cadmium thiolate, or triethylene diamine are less stable than those prepared with the zinc ethyl/water catalyst. Acid and oxygen initiate degradation			(1)
Decomposition temperature	K	Without stabilizer, the polymer viscosity falls rapidly	Above the melting point (498)	–
		Polymers initiated by zinc ethyl/water system with the stabilizers (polyamines in conjunction with zinc oxide or zinc hydroxychloride)	523	(1, 6)
Water absorption	%	24 h	0.03	(2)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Weight change	%	After immersion for 30 days		
		50% sulfuric acid, 121°C	−0.7	(2)
		15% sodium hydroxide, 121°C	−0.3	
		Benzene, 93°C	+4.0	
		Perchloroethylene, 121°C	7.0	
Creep	%	Room temperature, 34 MPa, 500 h	1	(2)
Important patents	—	Polymerization	U.S. Patent 3,365,431	(19)
		Stabilizer	Canadian Patent 736,026	(20)
		Stabilizer	Canadian Patent 778,848	(21)
Cost	—	—	Expensive	
Availability	Not commercially available (no commercial availability of ethylene sulfide monomer)			

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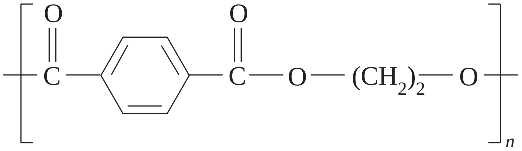
Poly(ethylene terephthalate)

JUDE O. IROH

ACRONYM, TRADE NAME PET, Dacron

CLASS Polyesters; linear aromatic polyesters; thermoplastics

STRUCTURE



MAJOR APPLICATIONS Fibers, films, barrier film, soft drink bottles (amorphous PET), film for compression molding polyethylene, polypropylene, and for replacement of commodity metals such as steel and aluminum.[1–3]

PROPERTIES OF SPECIAL INTEREST Mostly synthesized as semicrystalline thermoplastic. Amorphous PET is clear and is formed by quenching the polymer melt. Excellent film properties and easy to process. Impearmeable to air and hydrophobic.

PREPARATIVE TECHNIQUES Synthesized by condensation/step-growth polymerization between ethylene glycol and terephthalic acid. Low-viscosity and easily spinnable PET are synthesized by ester interchange. Dimethyl terephthalate is reacted with ethylene glycol in a 1:1.7 ratio at 0.020 atm and 160–230°C. Final reaction occur at 260–300°C under vacuum at 0.001 atm. Synthesis of PET is done by using aromatic sulphonates as catalysts[4–7]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular conformation	—	—	Nearly planar	—
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	192	—
Mark-Houwink parameters: *K* and *a*	$K = ml\,g^{-1}$ a = None	Solution viscometry, 30°C	$K = 3.72 \times 10^{-2}$ $a = 0.73$	(7, 8)
Solvent	—	—	*o*-Chlorophenol	(7, 8, 18)
Weight average molecular weight	$g\,mol^{-1}$	—	30,000–80,000	(7, 9, 10)
Unit cell	—	—	Triclinic:	—
Lattice constants	degrees	X-ray diffraction	$a = 4.56$ $b = 5.94$ $c = 10.75$ $\alpha = 98.5$ $\beta = 112$ $\gamma = 111.5$	(7, 11, 12, 13)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Number of chains per unit cell	–	–	1	(7, 11, 12, 13)
Unit cell density	$g\,cm^{-3}$	X-ray diffraction	1.501	(7, 11)
Measured density	$g\,cm^{-3}$	–	1.41	(7, 11)
Number of chains	–	–	1	(7, 11)
Number of monomers	–	–	1	(7, 11, 12, 13)
Glass transition temperature T_g	K	DSC	342–388	(5, 7, 14–16)
Melting temperature T_m	K	DSC	538	(5, 7, 14–16)
Heat of fussion ΔH	$kJ\,mol^{-1}$	DSC	24.1	(7, 14, 16, 17)
Breaking strength σ_B	MPa	Tensile	50	(1, 2, 15, 16)
Tensile (Young's) modulus E	MPa	–	1,700	(1, 2, 15, 16)
Flexural modulus (rigidity) E	MPa	3-point flexure	2,000	(1, 2, 15, 16)
Ultimate strain ε_B	%	Tensile	180	(1, 2, 15, 16)
Yield strain ε_Y	%	Tensile	4	(1, 2, 15, 16)
Impact strength	$J\,m^{-1}$	Notched Izod, ASTM D256-86	90	(1, 2, 15, 16)
Hardness	–	Rockwell	R105	(1, 2, 15, 16)
Deflection temperature	K	HDT		(1, 2, 15, 16)
		At 264 psi	336	
		At 66 psi	344	
Thermal expansion coefficient α	K^{-1}	TMA	9.1×10^{-5}	(18)
Water absorption	%	After 24 h	0.5	(1, 2, 16, 17)
Dielectric strength	$kV\,mm^{1}$	Thermal		(1, 2, 16, 17)
		1/8 in	15.7	
		1/16 in	22.1	
		Electrical; ASTM D149	26	
Dielectric constant	10^6 Hz	Thermal	3.2	(1, 2, 16, 17)
		Electrical; ASTM D150	3.3	
Volume resistivity	ohm cm	ASTM D257	0.1×10^{16}	(1, 2, 16, 17)
Power factor	10^6 Hz	D150	0.019	(1, 2, 16, 17)

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Poly(ferrocenyldimethylsilane)

IAN MANNERS

CLASS Inorganic and semi-inorganic polymers

STRUCTURE $[(C_5H_4)Fe(C_5H_4SiMe_2)]_n$

PROPERTIES OF SPECIAL INTEREST Low cost; ease of synthesis; interesting optical, magnetic, and electrical properties; and precursor to CSiFe solid state ceramic materials.

SYNTHESIS Poly(ferrocenyldimethylsilane) can be synthesized via the thermal ring opening polymeriztion (ROP) of the strained dimethylsila[1]ferrocenophane, $(C_5H_4)_2FeSiMe_2$.[1] Additionally, poly(ferrocenyldimethylsilane) can be prepared via anionic initiated ROP[2,3] or transition metal catalyzed ROP[4,5] of the strained [1]ferrocenophane.

PROPERTY	UNITS	CONDITION	VALUE	REFERENCE
UV-vis absorption, λ_{max}	nm	THF solution	430	(1)
UV-vis absorption coefficient, ε	$M^{-1}\,cm^{-1}$	THF solution	190	(1)
Glass transition temperature	K	DMA experiment	306	(1)
		DSC experiment	298	
Melting temperature	K	DSC experiment	395–418	(6)
Unit cell dimensions		For monomer $(C_5H_4)_2FeSiMe_2$		(7)
Lattice	–	–	Monoclinic	–
Monomers per unit cell	–	–	4	–
Cell dimensions	Å	–	$a = 7.438$	–
			$b = 10.322$	–
			$c = 15.575$	–
Cell angles	Degrees	–	$\alpha = 90$	–
			$\beta = 99.04$	–
			$\gamma = 90$	–

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Polygermanes

ROBERT WEST

ALTERNATIVE NAME Polygermylenes

CLASS Inorganic and semi-inorganic polymers

STRUCTURE $[-R_2Ge-]$

PROPERTIES OF SPECIAL INTEREST Polygermane polymers, with their main chain consisting entirely of germanium atoms, resemble polysilanes in showing properties resulting from delocalization of the σ-electrons along the polymer backbone. Thus the polygermanes have strong UV absorption bands, are thermochromic and photoactive, and become semiconducting when doped with SbF_5. Polysilane-polygermane copolymers have also been prepared, and are of interest as possible superlattice polymers. Listed below are known polygermanes and copolymers, with selected properties.

SYNTHESIS METHODS (a) Reaction of $GeCl_2 \cdot$ dioxane with RLi. (b) R_2GeCl_2, Na, toluene, 110°C. (c) Electroreduction.

POLYGERMANE	SYNTHESIS*	YIELD (%)	M_w	M_w/M_n	λ MAX.†	REFERENCE
$(Me_2Ge)_n$	a	25	31,000	–	–	(1)
$(Et_2Ge)_n$	b	–	3,400	1.2	303	(2)
$(n\text{-}Pr_2Ge)_n$	b	15	6,300	1.3	300	(2)
$(n\text{-}Bu_2Ge)_n$	b	25	423,000	1.74	333	(3)
			8,200	1.3		
	b	–	10,000	1.16	329	(4)
	b	52.5	6,800	1.6	320	(2)
	a	38	17,900	–	324	(1)
$(i\text{-}Bu_2Ge)$	b	2	3,900	1.12	330	(2)
$(n\text{-}Pent_2Ge)_n$	b	8.3	25,900	1.53	338	(5)
$(n\text{-}Hex_2Ge)_n$	b	20	15,100	1.5	325	(2)
	b	9.5	976,000	1.56	340	(5)
			6,500	1.12	–	(2)
	c	23	5,350	1.24	–	(5)
$(n\text{-}Oct_2Ge)_n$	b	70	4,437	–	–	(5)
$(PhGeMe)_n$	b	–	8,600	2.07	330	(4)
	b	–	5,000	1.4	327	(2)
$(n\text{-}BuGePh)_n$	b	–	19,900	–	355	(6)

*See "Synthesis Methods" above.
†UV absorption maxima in solution.

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POLYGERMANE-POLYSILANE COPOLYMER	SYNTHESIS*	YIELD (%)	M_w	M_w/M_n	λ MAX.†	REFERENCE
$(n\text{-HexGePh})_n$	b	3.3	12,500	—	355	(2)
$[(n\text{-Bu}_2\text{Ge})(\text{Me}_2\text{Si})2]_n$	b	7.9	13,000	—	312	(7)
$[(n\text{-Bu}_2\text{Ge})(n\text{-HexSiMe})_{4.3}]_n$	b	10	637,000	1.91	314	(3)
$[(\text{Ph}_2\text{Ge})_{1.2}(\text{Cy-HexSiMe})]_n$	b	22	509,000 5,600	1.55 1.5	317	(3)
$[(\text{Ph}_2\text{Ge})(n\text{-HexSiMe})_{1.6}]_n$	b	5	33,000 3,100	1.51 1.1	354, 305	(3)
$[(n\text{-Hex}_2\text{Ge})(n\text{-}Hex_2Si)]_n$	b	9	275,600	2.74	326	(5)
$[(n\text{-BuGePh})_{1.08}(\text{PhSiMe})]_n$	b	33	20,600	—	335	(7)

*See "Synthesis Methods" above.
†UV absorption maxima in solution.

OTHER PROPERTIES OF POLYGERMANES	REFERENCE
Photoresist properties of $(n\text{-Bu}_2\text{Ge})_n$	(8)
Luminescence of $(n\text{-Hex}_2\text{Ge})_n$	(9)
Flash photolysis of polygermanes	(2)
Polygermane-polysilane superlattice	(7, 10)
Conductivity of$(\text{PhGeMe})_n$ and $(n\text{-Bu}_2\text{Ge})$, doped with SbF_5	(4)
Hole transport properties	(11)

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Polyglycine

DOUGLAS G. GOLD AND WILMER G. MILLER

TRADE NAME Nylon 2

CLASS Polypeptides and proteins

STRUCTURE

$$\left[NH-CH_2-\overset{\overset{\displaystyle O}{\|}}{C} \right]$$

MAJOR APPLICATIONS Serves as a model for various proteins.

PROPERTIES OF SPECIAL INTEREST Two crystalline forms of polyglycine, I and II, have been observed. Form I is thought to have a β structure where the individual chains exist in a helical conformation and form sheets stabilized by hydrogen bonds.[1, 2] The individual chains in form II also have a helical conformation but are packed in a hexagonal lattice with a three-dimensional array of hydrogen bonds.[2]

SYNTHESIS The synthesis is similar to that of poly(γ-benzyl-L-glutamate). (See also the entry on *Poly(γ-benzyl-L-glutamate)* in this handbook.) It involves the conversion of the amino acid to the N-carboxyanhydride (NCA) monomer by reaction with phosgene gas followed by polymerization of the NCA with an appropriate initiator (e.g., triethylamine). Typical comonomers include other amino acid NCAs.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	g mol^{-1}	–	57	–
Typical molecular weight range	g mol^{-1}	–	<20,000	–
IR (characteristic absorption frequencies)	cm^{-1}	Polyglycine I Polyglycine II	3,308; 1,685; 1,636; 1,517; 1,432; 708 3,303; 1,644; 1,554; 1,420; 740	(3)
Solvents	–	25°C	Dichloroacetic acid, trifluoroacetic acid, concentrated Li^+ and NH_4^+ halides, phosphoric acid	(1, 4)
Nonsolvents	–	–	Water	–
Optical activity $[\alpha]_D$	–	–	0	–
Surface tension	mN m^{-1}	0°C	50.1	(5)
Axial translation per residue	Å	Form I Form II	3.5 3.1	(2) (1, 2)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Cost	US$ g^{-1}	25 mg – 1g	150	—
Availability	g	—	0.025–1	—
Suppliers	Sigma Chemical Co., P.O. Box 14508, St. Louis, Missouri 63178, USA. Aldrich Chemical Co., Inc., 1001 West Saint Paul Avenue, Milwaukee, Wisconsin 53233, USA.			

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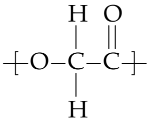
Poly(glycolic acid)

LICHUN LU AND ANTONIOS G. MIKOS

ACRONYM, TRADE NAME PGA, Dexon (Davis and Geck)

CLASS Poly(α-hydroxy esters)

STRUCTURE



MAJOR APPLICATIONS Sutures, drug delivery devices, and scaffolds for use in cell culture, transplantation, and organ regeneration.

PROPERTIES OF SPECIAL INTEREST Good biocompatibility; biodegradable mainly by simple hydrolysis; bioresorbable; good processability; a wide range of degradation rates, physical, mechanical, and other properties can be achieved by PGA of various molecular weights and its copolymers.

PREPARATIVE TECHNIQUES Practically useful high molecular weight PGA can be synthesized by a cationic ring opening polymerization of glycolide using organometallic compounds or Lewis acids as catalysts and alcohol as molecular weight and reaction rate control agent at high temperature and low pressure.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Degree of crystalline X_c	%	Dexon suture	46–52	(1)
Density ρ	$g\,cm^{-3}$	Typical range	1.5–1.64	(2)
		Complete amorphous	1.450	(3)
			1.50	(4)
		Complete crystalline	1.69	(5,6)
			1.707	(4)
Heat of fusion ΔH_f	$kJ\,mol^{-1}$	Complete crystalline	8.1	(7)*
			11.1	(8)
Entropy of fusion ΔS_f	$kJ\,K^{-1}\,mol^{-1}$	–	0.022	(9)

*Data calculated from $X_c(0.52) = \Delta H_f(72.3\,J\,g^{-1})/\Delta H_f$ (100% crystalline).

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Unit cell dimensions

Lattice	Space group	Monomers per unit cell	Cell dimension† (Å)			Packing density k	Chain conformation N^*P/Q	Reference
			a	b	c (fiber axis)			
Orthorhombic	$P2_12_12_1$	4	6.36	5.13	7.04	—	$3^*2/1$	(5)
Orthorhombic	*Pcmn*	4	5.22	6.19	7.02	0.81	$3^*2/1$	(5)
Orthorhombic	—	2	—	—	7	—	—	(6)

†Cell angles $\alpha = \beta = \gamma = 90°$.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Refractive index	—	Highly oriented fiber	$n_{\parallel} = 1.556$, $n_{\perp} = 1.466$	(6)
		Single crystal hedrite	$\alpha = 1.46$, $\beta = 1.50$, $\gamma = 1.66$	
Glass transition temperature T_g	K	$M_w > 20{,}000$	318	(7)
		$M_w = 50{,}000$	309	(1)
Melting point T_m	K	$M_w > 20{,}000$	495	(7)
		$M_w = 50{,}000$	483	(10)
		$M_w = 50{,}000$	503	(1)
		—	500–503	(4)
			506	(5)
Heat capacity C_p	$J\,K^{-1}\,mol^{-1}$	Crystalline PGA in temp. range = 0–318 K	—	(3)*
		$T = 273.15$	115.0	(3)
		$T = 298.15$	121.4	(3)
		$T = 318.0$ (T_g)	126.5	(3)
		Molten PGA, $T = 318.0$–550.0 K	226.5–243.4	(3)
		Predicted results in temp. range = 0–1,000 K	—	(11)
Solvent	Glycolide at high temperature			(12)
	Hexafluoroisopropanol at room temperature			(13)
	Phenol/trichlorophenol at $T = 190°C$			(12, 14)
Inherent viscosity	$dl\,g^{-1}$	In hexafluoroisopropanol	0.5–1.6	(2)
		In phenol/trichlorophenol at $T = 30°C$	0.35	(14)
Water absorption	%	250 μm films in 0.2 M pH 7 phosphate buffer	28	(1)
Apparent permeability K	$m^4\,N^{-1}\,s^{-1}$	Prewetted nonwoven discs	4.29×10^{-10}	(15)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Degradation rate	—	In vitro In vivo	— —	(13, 15–17) (2, 17)
Decomposition temperature T_d	K	$M_w = 50{,}000$, $X_c = 0.52$ at heating rate $= 20°C\ min^{-1}$ under nitrogen	527	(10)
G factor	Under ^{60}Co irradiation at $T = 25°C$, chain scission factor approximately equal to cross-linking factor			(14)
Tensile strength	MPa	Dexon plus (PGA multifilament) Gauge 0 Gauge 1	 339 394	(18)
Tenacity	MPa	Melt-spun fiber (diameter = 15–25 μm) Dexon suture	690–1,380 6,050	(2) (16)
Knot pull strength	MPa	Size 3/0 suture	343	(2)
Straight pull strength	MPa	Size 3/0 suture	536	(2)
Knot/straight tenacity	%	Melt-spun fiber (diameter = 15–25 μm)	50–80	(2)
Elongation at break	%	Melt-spun fiber (diameter = 15–25 μm)	15–35	(2)
Confined compressive modulus	MPa	Prewetted nonwoven discs	2.86×10^{-3}	(15)
Aggregate modulus	MPa	Prewetted nonwoven discs	1.22×10^{-3}	(15)

*Data in reference (3) referred to ($CH_2-COO-CH_2-COO$).

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Poly(hexene-1)

D. R. PANSE AND PAUL J. PHILLIPS

ACRONYMS PHE, PHEX

CLASS Poly(α-olefins)

STRUCTURE OF REPEAT UNIT $[-CH_2-CH(CH_2CH_2CH_2CH_3)-]$

MAJOR APPLICATIONS Comonomer for ethylene and 4-methyl pentene-1, flow modifier.

PREPARATIVE TECHNIQUE Coordination polymerization: (a) bis(cyclopentadienyl)zirconium dichloride + methylaluminoxane catalyst;[1] (b) soluble magnesium-titanium catalyst in xylene + diethylaluminium chloride cocatalyst at 40°C for 420 min;[2] (c) $MgCl_2$ supported $TiCl_3$ catalyst.[3]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Typical comonomers used	–	–	Ethylene, 4-methyl pentene-1,1-pentene	–
Molecular weight (of repeat unit)	g mol^{-1}	–	84.16	–
Stereoregularity	–	Soluble magnesium-titanium catalyst in xylene + diethylaluminium chloride cocatalyst	Mainly isotactic	(2)
Typical molecular weight range	g mol^{-1}	1. Stereorigid metallocene catalysts (number average mol. wt.)	<30,000	(4)
		2. $MgCl_2$ supported $TiCl_3$ catalyst (weight average mol. wt.)	100,000	(3)
Typical polydispersity index	–	1. Stereorigid metallocene catalysts	2–3	(4)
		2. Heterogeneous $MgCl_2$ supported $TiCl_3$ catalyst	5–11	(3)
		3. Soluble magnesium-titanium catalyst	2.0–2.7	(2)
Solvents	–	1. For amorphous polymer at ambient temperature	Saturated and aromatic hydrocarbon solvents	(5)
		2. For crystalline isotactic polymer at 135°C	Decalin	
Nonsolvents	–	For crystalline isotactic polymer at ambient temperature	Saturated and aromatic hydrocarbon solvents	(5)
Theta temperature	K	Phenetole/VM	334.3	(6)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Characteristic ratio	–	Method: viscometry at 27°C	13.0	(7)
Lattice	–	None given	Monoclinic	(8)
Unit cell dimensions	Å	Isotactic polymer	$a = 22.2$ $b = 8.89$ $c = 13.7$	(8)
Unit cell angles	Degrees	Isotactic polymer	$\alpha = \beta = 90$ $\gamma = 94.5$	(8)
Monomers per unit cell	–	Isotactic polymer	14	(8)
Helix conformation	–	Isotactic polymer	7_2	(8)
Crystalline density	g cm^{-3}	Isotactic polymer	0.83	(8)
Glass transition temperature	K	Calorimetry	215 223	(9) (10)
Melting temperature	K	None given	<293	(5)
Heat capacity	kJ K^{-1} mol^{-1}	Temperature (K) 100 200 250 290	 0.059 (amorphous) 0.112 0.160 (amorphous) 0.1749 (amorphous)	(10)
Polymers with which compatible	–	Single T_g criteria	1-Pentene	(11)
WLF constants: C_1 and C_2	–	None given	$C_1 = 17.4$ $C_2 = 51.6$	(12)
Refractive index increment	ml g^{-1}	Cyclohexane at 25°C Toluene at 25°C	−0.063 −0.042	(13)

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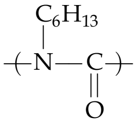
Poly(*n*-hexyl isocyanate)

JAGATH K. PREMACHANDRA, CHANDIMA KUMUDINIE, AND JUNZO MASAMOTO

ACRONYM PHIC

CLASS Poly(isocyanates); N-substituted 1-nylons

STRUCTURE



MAJOR APPLICATIONS An ideal example of a polymer model for a semi-rigid macromolecular chain material amenable to physical studies.

PROPERTIES OF SPECIAL INTEREST Polymer model for a semi-flexible macromolecular chain material. Stiff-chain solution characteristics due to helical configuration;[1, 2] liquid crystalline properties;[3] and molecular weight dependent chain dimensions in solution.[4]

OTHER POLYMERS SHOWING THIS SPECIAL PROPERTY Poly(*n*-butyl isocyanate), poly(γ-benzyl-L-glutamate)

Preparative techniques*

Polymerization Process	Conditions	Reference
Anionic	Temp.: -58°C; catalyst: NaCN in dimethylformamaide; solvent: benzene	(5)
Anionic	Temp.: -78 to -100°C; catalyst: NaCN in dimethylformamaide; solvent: toluene	(6)
Coordination	Catalysts: $TiCl_3(OCH_2CF_3)$, $TiCl_3(OCH_2CF_3)$-$(THF)_2$	(7)
Coordination	Catalysts: $C_pTiCl_2N(CH_3)_2$, $C_p = \eta^5$-cyclopentadienyl; 1 equivalent of Lewis base per monomer; no solvent	(8)

*For synthesis of the monomer, *n*-hexyl isocyanate, see reference (2).

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Ceiling temperature	K	—	316.4	(7)
			251	(9)
Typical comonomers	—	—	Styrene, methyl methacrylate for block copolymer	(10)
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	127	—

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Typical molecular weight range of polymer	$g\,mol^{-1}$	–	2.4×10^4–5.14×10^5 $>10^6$ 4×10^3–7×10^6	(11) (12) (13)
Typical polydispersity index (M_w/M_n)	–	–	1.4 1.05–1.2 1.05–1.1	(14) (15) (16)
IR (characteristic absorption frequencies)	cm^{-1}	Solid state	C=O absorption at 1,700	(17)
		Solid state	C=O absorption at 1,709	(5)
		Dilute solution in tetrachloroethane	C=O absorption at 1,700	(17)
		Solid state	Disubstituted amide at 1,282 and 1,390	(5)
UV (absorption maxima at the high wavelength band, λ_{max})	nm	In *n*-hexane at room temperature	252	(18)
Extinction coefficient	$L\,mol^{-1}\,cm^{-1}$	In *n*-hexane at room temperature	4,572	(18)
NMR	^{13}C NMR, 300- and 500-MHz instrument, spin-lattice and spin-spin relaxation times and nuclear Overhauser enhancements of carbon atoms in or near the backbone of the extended-chain polymer			(19)
	NMR line-width measurement			(20)
	^1H NMR			(21)
Solvents	Aromatic and chlorinated hydrocarbons			(4, 5)
	Hexane, *n*-butyl benzene, toluene, many solvents in the presence of trifluroacetic acid			(4)
Nonsolvents	Methanol, cyclohexyl benzene, dodecyl benzene, higher paraffins (number of carbons > 6)			(4)
Theta temperature θ	K	In toluene	289.4	(22)
		In methanol/toluene (19.5% v/v), turbidity point method	298	(4)
		In methanol/carbon tetrachloride	298	(4)
		(18.5% v/v), turbidity point method	297	(23)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Second virial coefficient	$mol\,cm^3\,g^{-2}$	In tetrahydrofuran at 25°C, $M_w = (3.8 \times 10^4$–$4.24 \times 10^5)\,g\,mol^{-1}$, light scattering	$(9.7–16.6) \times 10^{-4}$	(4)
		In toluene at 34.4°C, $M_n = (3.9 \times 10^4$–$3.85 \times 10^5)\,g\,mol^{-1}$, osmometry	$(3.66–8.34) \times 10^{-4}$	(4)
		In tetrachloroethane, $M_w = 9.6 \times 10^4\,g\,mol^{-1}$, in anisotropic phase, light scattering	1.8×10^{-3}	(14, 24)
		In tetrachloroethane, $M_w = 5.6 \times 10^4\,g\,mol^{-1}$, in isotropic phase, light scattering	1.8×10^{-3}	(14, 24)
		In tetrachloroethane, $M_w = 7 \times 10^4\,g\,mol^{-1}$, in anisotropic phase, osmometry	1.9×10^{-3}	(14, 24)
		In tetrachloroethane, $M_n = 4 \times 10^4\,g\,mol^{-1}$, in isotropic phase, osmometry	3.1×10^{-3}	(14, 24)
		In toluene at 34.4°C, $M_n = 7.9 \times 10^4\,g\,mol^{-1}$, osmometry	7.8×10^{-4}	(23)
		In hexane at 25°C, $M_w = 6.8 \times 10^4\,g\,mol^{-1}$, light scattering	9.8×10^{-4}	(23)
		In hexane at 25°C, $M_w = 4.63 \times 10^6\,g\,mol^{-1}$, light scattering	7.5×10^{-4}	(23)
		In hexane at 25°C, $M_w = 7.24 \times 10^6\,g\,mol^{-1}$, light scattering	5.4×10^{-4}	(23)
		$M_w = (1.1 \times 10^5$–$1.06 \times 10^6)\,g\,mol^{-1}$, light scattering	$(5.97–6.49) \times 10^{-4}$	(16)
		In tetrahydrofuran, $M_w = (1.46$–$3.55) \times 10^5\,g\,mol^{-1}$, light scattering	$(6.9–8.2) \times 10^{-4}$	(25)

Mark–Houwink parameters: *K* and *a*

Solvent	Temp. (°C)	Molecular weight ($g\,mol^{-1}$)	$K_m \times 10^5$ ($dl\,g^{-1}$)	*a*	Reference
Toluene	25	$M_w = (0.038–4.3) \times 10^5$	2.48	1.05	(4)
Methanol/toluene	25	$M_w = (0.038–4.3) \times 10^5$	2.72	1.04	(4)
Carbon tetrachloride	25	$M_w = (0.038–4.3) \times 10^5$	1.52	1.10	(4)
Trifluro acetic acid/carbon tetrachloride	25	$M_w = (0.038–4.3) \times 10^5$	5.68	0.96	(4)
Tetrahydrofuran	25	$M_w = (0.038–4.3) \times 10^5$	2.20	1.06	(4)
Chloroform	25	$M_w = (0.038–4.3) \times 10^5$	4.99	0.97	(4)
Dichloromethane	20	$(0.24–5.14) \times 10^5$	6.6	0.923	(11)
Hexane	25	$(0.68–3.9) \times 10^5$	100	1.2	(23)
Hexane	25	$>10^6$	8,800	0.77	(23)
Hexane	25	$(0.091–2.3) \times 10^6$	540	0.97	(26)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Huggins constant	–	Toluene at 25°C	0.346	(4)
		Carbon tetrachloride at 25°C	0.341	(4)
		Chloroform at 25°C	0.319	(4)
		Tetrahydrofuran at 25°C	0.331	(4)
		1.5% acetic acid/carbon tetrachloride	0.328	(4)
		1.5% methanol/toluene	0.326	(4)
		Hexane at 25°C, $M_w = (0.68–3.34) \times 10^5$ g mol^{-1}	0.38	(23)
		Hexane at 25°C, $M_w = 7.24 \times 10^6$ g mol^{-1}	0.50	(23)
		Carbon tetrachloride, $M_w = 3.55 \times 10^5$ g mol^{-1}	0.56	(25)
		Benzene, $M_w = 3.55 \times 10^5$ g mol^{-1}	0.51	(25)
		Tetrahydrofuran, $M_w = 3.55 \times 10^5$ g mol^{-1}	0.43	(25)
		Tetrahydrofuran/dimethylformamide (4:1), $M_w = 3.55 \times 10^5$ g mol^{-1}	0.75	(25)
		Chloroform	1.10	(25)
Characteristic ratio $\langle r^2 \rangle_0/nl^2$	–	–	410	(27)
Radius of gyration	Å	In tetrahydrofuran at 25°C, $M_w = (0.38–4.3) \times 10^5$ g mol^{-1}	162-966	(4)
		In tetrachloroethane, $M_w = 9.6 \times 10^4$ g mol^{-1}, in anisotropic phase	315	(14)
		In tetrachloroethane, $M_w = 5.6 \times 10^4$ g mol^{-1}, in isotropic phase, light scattering	180	(14)
		In butyl chloride, light scattering, $M_w = (0.043–2.1) \times 10^6$ g mol^{-1}	300–2,190	(28)
Monomer projection length	Å	In carbon tetrachloride	~2.1–1.1	(4)
		In toluene	~2.1–1.0	
		In chloroform	~2.0–0.7	
Persistence length	Å	In 1-chloronaphthalene at 25°C; chain diameter $d = 10.3$ Å	230	(29)
		In 1-chloronaphthalene at 25°C, $d = 16.4$ Å	200	(29)
		In 1-chloronaphthalene at 45°C, $d = 10.3$ Å	190	(29)
		In 1-chloronaphthalene at 45°C, $d = 16.4$ Å	165	(29)
		In 1-chloronaphthalene at 90.2°C, $d = 10.3$ Å	110	(29)
		In 1-chloronaphthalene at 90.2°C, $d = 16.4$ Å	95	(29)
		In 1-chloronaphthalene at 110.8°C, $d = 10.3$ Å	90	(29)
		In 1-chloronaphthalene at 110.8°C, $d = 16.4$ Å	80	(29)
		In chloroform	200	(30)
		In dichloromethane	185	(11)
		In dichloromethane at 20°C	210	(31)
		In hexane	420	(23)
		In toluene	375	(11)
		In toluene at 10°C	410	(31, 37)
		In toluene at 25°C	370	(31, 37)
		In toluene at 40°C	340	(31, 37)
		In tetralin	400	(32)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Persistence length	Å	In tetrahydrofuran	425	(4)
		In tetrahydrofuran	400-500	(33)
		In butyl chloride	450	(28)
Lattice	—	Only a few *d* spacings were given	—	(34, 35)
Chain conformation	In the solid state by X-ray scattering: 12_5 helix			(34)
	A helical rodlike conformation at low molecular weights and a transition to random-coil conformation at high molecular weight			(1, 4)
Degree of crystallinity	%	X-ray diffraction	Low order of crystallinity	(5)
Density	$g\,cm^{-3}$	—	1.000	(14, 36)
Partial specific volume	$cm^3\,g^{-1}$	In toluene at 25°C	0.987	(37)
		In toluene at 40°C	1.002	
		In toluene at 10°C	0.972	
		In dichloromethane at 20°C	0.992	
Glass transition temperature	K	By thermally stimulated discharge currents	223	(38)
		Hydrosilation cross-linked, DSC	258	(39)
		Copolymer with 10 mol% allyl composition, DSC	273	(39)
Melting point	K	DTA-DSC, Ar atmosphere, heating rate = $10°C\,min^{-1}$	~428	(17)
		$M_w = 9.6 \times 10^4\,g\,mol^{-1}$	468	(40)
			468	(5)
			473	(41)
Mesomeric transition temperatures	K	Crystalline-nematic transition	438	(41)
		Crystalline-nematic transition, $M_w = 9.4 \times 10^4$	450	(40)
Sub-T_g transition temperatures	K	Chain skeleton rearrangement relaxations (or transition), $M_w = 9.4 \times 10^4\,g\,mol^{-1}$	293 and 313	(42)
			393	(40)
Softening temperature	K	—	393	(5)
Tensile modulus	MPa	At 23°C, strain rate = $8.3 \times 10^{-4}\,s^{-1}$	~420	(43)
		At −100°C	1,600	(44)
		At −40°C	1,000	(44)
		At 20°C	300	(44)
		Highly oriented fibers, orientation angle = 4.6°, room temperature, strain rate = $10\,mm\,min^{-1}$	~4,000	(45)
Theoretical axial modulus	MPa	Side chain reduced the axial modulus of rigid-chain polyamides by ~90%	~6,000	(45)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength	MPa	At 23°C, strain rate = $8.3 \times 10^{-4}\ s^{-1}$	~10	(43)
		Highly oriented fibers, room temperature, strain rate = 10 mm min^{-1}	~200	(45)
Maximum extensibility	%	At 23°C, strain rate = $8.3 \times 10^{-4}\ s^{-1}$	~8	(43)
		Highly oriented fibers, room temperature, strain rate = 10 mm min^{-1}	~6.6	(45)

Mechanical properties of cross-linked PHIC[46, 47]

Conditions	Properties		
	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Uncross-linked, 10% allyl concentration	140	10.6	11.0
Cross-linked, high-temp., hydrosilation	30	2.6	46.0
Oriented, high-temp., hydrosilation	260	15.6	12.5
Crosslinker: hydrido-oligo (dimethylsiloxane)			
Unoriented	30	4.55	166.6
Oriented, uniaxial //			
Extension ratio 35%	83	9.72	84.4
Extension ratio 70%	233	18.76	65.5
Extension ratio 100%	310	24.13	49.4
Oriented, uniaxial ⊥			
Extension ratio 20%	49	5.77	79.5
Extension ratio 50%	27	3.48	59.2
Oriented, biaxial			
Extension ratio 20%	62	13.71	157.5
Cross-linker: hexamethyl-trisiloxane			
Unoriented	16	7.05	172.7
Oriented, uniaxial //			
Extension ratio 80%	103	23.60	80.8
Extension ratio 120%	309	34.21	33.8
Extension ratio 140%	394	39.82	37.1

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Entanglement molecular weight M_c	g mol^{-1}	–	6,350	(27, 33)
Refractive index increment dn/dc	ml g^{-1}	In *n*-butyl chloride at 25°C, $\lambda_0 = 546$ nm	0.092	(13)
		In *n*-hexane at 25°C, $\lambda_0 = 546$ nm	0.134	(23)
		In tetrahydrofuran, $\lambda_0 = 436$ nm	0.100	(48)
		In tetrahydrofuran, $\lambda_0 = 546$ nm	0.097	(48)
		In tetrahydrofuran, $\lambda_0 = 436$ nm	0.099	(33)
		In tetrahydrofuran at 25°C, $M_w = 3.8 \times 10^4$ g mol^{-1}	0.088	(4)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Refractive index increment dn/dc	$ml\,g^{-1}$	In tetrahydrofuran at 25°C, $M_w = 6.8 \times 10^4\,g\,mol^{-1}$	0.0900	(4)
		In tetrahydrofuran, $M_w = 7.2 \times 10^4$ and $7.9 \times 10^4\,g\,mol^{-1}$	0.0910	(4)
		In tetrahydrofuran, $M_w = (1.11, 1.35, 1.62, 2.04, 3.12, \text{and } 4.24) \times 10^5\,g\,mol^{-1}$	0.0934	(4)
Dielectric constant ε'	–	In toluene at 292.2 K, 21.4% polymer (w/w), frequency range $\sim(2\text{–}1 \times 10^5)$ Hz	~(10–120)	(49)
Dielectric loss ε''	–	In toluene at 292.2 K, 21.4% polymer (w/w), frequency range $\sim(2\text{–}1 \times 10^5)$ Hz	~(4–24)	(49)
Dielectric critical frequency f_c	Hz	In toluene at 292.2 K, 21.4% polymer (w/w), frequency range $\sim(2\text{–}1 \times 10^5)$ Hz	~400	(49)
Optical activity: specific rotation $[\alpha]_D$	Degree	Poly((R)-1-deuterio-*n*-hexyl isocyanate) at the sodium *d*-line in dilute solution of chloroform at:		
		10°C	−450	(50)
		25°C	−367	(50)
		47°C	−258	(50)
		Poly((R)-1-deuterio-*n*-hexyl isocyanate), degree of polymerization = 6,800:		
		In chloroform and in hexane, (60 to −20°C)	~3 fold increase in $[\alpha]_D$	(51)
		In chloroform, (70 to −30°C)	~(−550 to −150)	(52)
		Poly((R)-1-deuterio-*n*-hexyl isocyanate) and poly((R)-2-deuterio-*n*-hexyl isocyanate), in dicloromethane, in 1-chlorobutane, in toluene and in hexane, (100 to −20°C)	$[\alpha]_D$ increases with decreasing temperature	(53)
		Copolymer of 99.5% *n*-hexyl isocyanate and 0.5% (R)-2, 6-dimethylheptyl isocyanate, (40 to −20°C) (for *n*-hexane ~ − 5°C, for *n*-octane ~ 10°C)	Sudden increase in $[\alpha]_D$	(54)
Decomposition temperature	K	TGA, N_2 atmosphere, heating rate = $20°C\,min^{-1}$	463	(3)
		TGA, heating rate = $10°C\,min^{-1}$	~453	(17)
		At polymer melting point	468	(5)

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Poly(*n*-hexyl isocyanate)

Intrinsic viscosity

Molecular weight ($g\,mol^{-1}$)	Solvent	Temp. (°C)	$[\eta]$ ($dl\,g^{-1}$)	Reference
$M_v = (1.01\text{–}2.78) \times 10^5$	Toluene	25	4.4–12.9	(29)
$M_v = (1.01\text{–}2.78) \times 10^5$	1-Chloronaphthalene	25	3.4–9.1	(29)
$M_v = (1.01\text{–}2.78) \times 10^5$	1-Chloronaphthalene	45	3.1–7.6	(29)
$M_v = (1.01\text{–}2.01) \times 10^5$	1-Chloronaphthalene	90.2	2.0–3.4	(29)
$M_v = (1.01\text{–}2.78) \times 10^5$	1-Chloronaphthalene	110.8	1.6–3.8	(29)
$M_w = 3.55 \times 10^4$	Carbon tetrachloride	—	12.1	(25)
$M_w = 3.55 \times 10^4$	Benzene	—	11.5	(25)
$M_w = 3.55 \times 10^4$	Tetrahydrofuran	—	10.0	(25)
$M_w = 3.55 \times 10^4$	Tetrahydrofuran-dimethylformamide (4:1)	—	7.8	(25)
$M_w = 3.55 \times 10^4$	Chloroform	—	7.3	(25)
$M_w = 6.5 \times 10^4$	Toluene	25	2.6	(17)
$M_w = 6.5 \times 10^4$	Chloroform	—	2.2	(17)
$M_w = 6.5 \times 10^4$	Methanol/toluene (19.5 v/v%)	—	2.38	(17)

Pyrolyzability

	Conditions	Observation	Reference
Nature of product	Direct pyrolysis mass spectrometry	Cyclic trimer of *n*-hexyl isocyanate as the principle decomposition product, and small amounts of hexyl isocyanate	(3)
	Thermal degradation tandem mass spectrometry	Principal pyrolysis product is the neutral trimer, minor amounts of monomer	(55)
Amount of product	At 138°C in xylene solution (conc. 0.1%)	Cyclic trimer of *n*-hexyl isocyanate	(5)
		Relative viscosity reduced quickly (within 30 min)	(5)
Impurities remaining	At room temperature in dimethylformamide	Depolymerization occurs in the presence of anionic initiator such as sodium cyanide	(5)

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Poly(hydridosilsesquioxane)

RONALD H. BANEY

ACRONYMS, ALTERNATIVE NAMES, TRADE NAME HSQ, LPHSQ, hydridosilsesquioxane, hydrogen silsesquioxane, polyhydrosilsesquioxane, FOx® (Dow Corning Corp.)

CLASS Polysiloxanes (siloxane ladder polymers)

STRUCTURE The structure has not been reported in the literature.

MAJOR APPLICATIONS Interlayer dielectrics, high-temperature resins.

PROPERTIES OF SPECIAL INTEREST Very high thermal stability (>500°C) and good dielectric properties.

RELATED POLYMERS Polyalkylsilsesquioxane and poly-*co*-silsesquioxanes. There are many references to these classes of materials,[1] but they are generally poorly characterized. Thus, they are not included in this handbook.

Process

Acronym	Process	Reference
PHSQ	Hydrolysis of $HSiCl_3$ with sulfuric acid in aromatic solvents	(2)
LPHSQ	Pre-aminolysis of $HSiCl_3$ with 1,4-phenylene diamine (PDA) (2:1 mole ratio) and then hydrolysis in acetone-toluene solvent mixtures	(3)
LPPMHSQ	An oligomer of LPHSQ was reacted with an oligomer of $MeSiO_{3/2}$ prepared in the same way as LPHSG	(3)

Characterization of hysdridosilsesquioxanes

Material	Solubility	GPC M_w	IR (cm^{-1})	Density ($g\,cm^{-3}$)	Dielectric constant (1 MHz)	Reference
PHSQ, 400°C cure	–	–	–	1.7	3.0	(4)
LPHSQ	Toluene	10^5–10^6	1,076, 1,132 (Si-O-Si) 2,257 (Si-H) 835 (Si-OH)	–	–	(3)
LBPMHSQ	Toluene	10^6	1,113 (Si-O-Si) 2,259 (Si-H) 835 (Si-OH) 769, 1,274 (Si-Me)	–	–	(3)

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Poly(4-hydroxy benzoic acid)

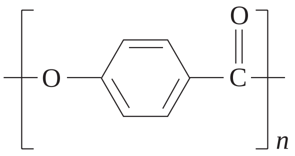
TAREK M. MADKOUR

ACRONYM, TRADE NAME PHBA, Ekonol® (Norton)

CLASS Polyesters

SYNTHESIS Polycondensation

STRUCTURE



MAJOR APPLICATIONS A component in a family of random copolymers that show thermotropic liquid crystalline behavior and are marketed as structural materials.

PROPERTIES OF SPECIAL INTEREST Intractable polymer with no melting behavior below temperatures of significant degradation. It polymerizes directly into the crystalline state, thus showing high tensile stiffness, low dielectric constant, and dimensional stability at high temperatures.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	120.11	(1)
Typical molecular weight range	$g\,mol^{-1}$	–	1,000–20,000	(2)
Infrared bands (frequency)	cm^{-1}	–	3,440; 1,735; 1,600; 1,540; 1,420; 880	(3)
^{13}C NMR bands	–	Solid state from CP/MAS data		(4)
		Phenoxy	155.0	
		Carboxyl	162.9	
Thermal expansion coefficient	K^{-1}	–	5.04×10^5	(5)
Characteristic ratio $\langle r^2 \rangle_0 / nl^2$	–	Calculated at 300 K, for a chain with 30 monomeric units	20	(6)
Persistence length	Å	Calculated at 300 K, for a chain with 30 monomeric units	65	(6)
Radius of gyration	Å	Calculated at 300 K, for a chain with 30 monomeric units	42	(6)

Poly(4-hydroxy benzoic acid)

Unit cell dimensions[1,7]

Isomer	Lattice	Space group	Cell dimension (Å)			Chain confirmation	Density (g cm^{-3})
			a	*b*	*c*		
Phase I	Ortho	$Pbc2_1$	7.42	5.70	12.45	$6^*2/1$	1.51
Phase II	Ortho	$Pbc2_1$	3.83	11.16	12.56	$6^*2/1$	1.48
Phase III	Ortho	—	9.2	5.3	12.4	$6^*2/1$	—

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Unit cell contents (number of repeat units)	—	—	4	(8)
Unit cell volume	$Å^3$	—	532	(8)
Glass transition temperature	K	—	434	(9)
Crystal–plastic crystal transition temperature	K	—	623	(7, 10)
Enthalpy of fusion	kJ mol^{-1}	—	4.204	(10)
Plastic crystal – nematic transition temperature	K	—	718	(7)
Heat capacity C_p	kJ K^{-1} mol^{-1}	Under constant pressure		(9)
		170 K	0.071	
		300 K	0.123	
		400 K	0.164	
		434 K	0.176	
Specific heat increment	kJ K^{-1} mol^{-1}	At T_g	0.034	(9)
Elastic modulus	MPa	—	6,896	(5)
Flexural strength	MPa	—	75.8	(5)
Dielectric strength	kV/mm	—	26	(5)
Volume resistivity	ohm cm	Unfilled samples	1×10^{15}	(5)
Dissipation factor	—	—	2×10^{-4}	(5)
Thermal conductivity k	W m^{-1} K^{-1}	—	0.013	(5)
Intrinsic viscosity $[\eta]$	—	Polymerized for 3 h in water bath: Solvent / Mesogenic character		(3)
		Xylene / Smectic	0.0321	
		Toluene / Smectic-nematic	0.0330	
		Benzene / Smectic	0.0355	
		Nitrobenzene / Nonmesogenic	0.0384	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Maximum use temperature	K	—	723	(5)
TGA weight loss	%	Heating rate 10°C per minute		(3)
		250°C	2.97	
		300°C	4.80	
		350°C	5	
		400°C	11.45	
		500°C	22.9	
		600°C	98.43	

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Poly(hydroxybutyrate)

ISAO NODA, ROBERT H. MARCHESSAULT, AND MIKIO TERADA

ACRONYMS, ALTERNATIVE NAMES, TRADE NAMES PHB, poly(3-hydroxybutyrate), P(3HB)*, poly(oxy-1-oxo-3-methyl-trimethylene), Biopol™

CLASS Chiral aliphatic polyesters

STRUCTURE $[-O-CH(CH_3)-CH_2-CO-]$

MAJOR APPLICATIONS In bacteria, PHB is a carbon reserve. The purified product is used as biodegradable packaging (bottles, containers, sheets, films, laminates, fibers, and coatings), especially as a copolymer of β-hydroxybutyrate and β-hydroxyvalerate. In biomedical applications, it is an excipient, a prosthetic material, etc. In organic syntheses, it provides chiral synthons.

PROPERTIES OF SPECIAL INTEREST Biocompatibility and biodegradability. Biologically produced PHB is a semicrystalline isotactic stereoregular polymer of 100% *R* configuration that allows a high level of degradability. PHB is obtained by fermentation of bacteria capable of biosynthesizing polyesters as energy storage media. It can be completely biodegraded by numerous microorganisms. Synthetic racemic stereoblock structures degrade more slowly than the bacterial products. Copolymers, such as poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), are also available.

PREPARATIVE TECHNIQUES The 100% *R* configuration isotactic polymers are prepared by bacterial fermentation. Production in transgenic plants promises an agrotechnological production method similar to that for starch. Optically active synthetic polymer can also be prepared either by starting with optically active β-butyrolactone or by using a stereoselective catalyst with racemic β-butyrolactone. In vitro enzymatic synthesis using cloned synthase and (*R*)-β-hydroxybutyryl-CoA monomer.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	86.09	–

Tacticity (stereoregularity)

Catalyst	Monomer	Isotactic dyads (%)	Syndiotactic dyads (%)	Reference
Alcaligenes eutrophus	(*R*)-β-hydroxybutyryl-CoA	100	0	(1)
$ZnEt_2/H_2O$	(*S*)-β-butyrolactone	100	0	(1)
1-Ethoxy-3-chlorotetrabutyldistannoxane	(*R*)-β-butyrolactone	94	6	(2)
Methylaluminoxane	(*R,S*)-β-butyrolactone	32 ± 5	68 ± 5	(3)
1-Ethoxy-3-chlorotetrabutyldistannoxane	(*R,S*)-β-butyrolactone	30	70	(2)

*P(3HB-co-3HV) is a copolymer with valerate.

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Polydispersity index (M_w/M_n)

Bacterial products in vivo depending on bacterial strain and carbon source[4]

Strain	Carbon source	Method	M_w	M_w/M_n
Alcaligenes eutrophus	Fructose	GPC	7.37×10^5	1.9
Alcaligenes eutrophus	Butyric acid	GPC	4.32×10^5	2.1
Bacillus megaterium	Glucose	GPC	1.66×10^5	2.9
Zoogloea ramigera	Glucose	GPC	5.42×10^5	2.5

Fractionated bacterial products in vivo*[5]

Sample code	M_w	Method	M_n	Method	M_w/M_n
A-12	3.99×10^6	Light scattering	—	—	—
A-22	1.64×10^6	Light scattering	—	—	—
AB-12	1.35×10^6	Light scattering	—	—	—
AB-22	8.57×10^5	Light scattering	—	—	—
B-23	6.30×10^5	Light scattering	2.80×10^5	Osmotic pressure	2.25
B-32	5.33×10^5	Light scattering	2.77×10^5	Osmotic pressure	1.92
B-42	3.74×10^5	Light scattering	2.25×10^5	Osmotic pressure	1.66
B-5	2.36×10^5	Light scattering	1.91×10^5	Osmotic pressure	1.24
B-62	2.29×10^5	Light scattering	1.60×10^5	Osmotic pressure	1.43
B-72	1.15×10^5	Light scattering	8.55×10^4	Osmotic pressure	1.35

*Strain: *Azotobacter vinerand* ATCC 12837. Carbon source: sucrose.

Bacterial products in vitro

Enzyme	Monomer	Method	M_w	Reference
PHB synthase	(*R*)-β-hydroxybutyryl-CoA	GPC	1.3×10^7	(6)
Porcine pancreatic lipase	(*R,S*)-β-butyrolactone	MALDI-TOF MS*	256 ~ 1,045	(7)
Pseudomons cepacia lipase	(*R,S*)-β-butyrolactone	MALDI-TOF MS*	643 ~ 681	(7)

*MALDI-TOF MS: matrix-assisted laser desorption and ionization time of flight mass spectroscopy.

Synthetic products

Catalyst	Monomer	M_w*	M_w/M_n	Isotactic dyads (%)	Reference
ZnEt2/H20	(*S*)-β-butyrolactone	20,000	1.5	0	(1)
Methylaluminoxane	(*R,S*)-β-butyrolactone	130,000	8.1	79 ± 5	(3)
1-Ethoxy-3-chlorotetrabutyldistannoxane	(*R*)-β-butyrolactone	424,000	2.4	94	(2)
1-Ethoxy-3-chlorotetrabutyldistannoxane	(*R,S*)-β-butyrolactone	261,000	1.8	30	(2)

*Determined by GPC.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
IR (characteristic absorption frequencies)	cm^{-1}	C=O stretching	1,754	(8)

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IR (characteristic absorption frequencies) (*continued*)

Frequency (cm^{-1})	Relative intensity	Polarization	Interpretation
2,990	Shoulder	⊥	CH_3
2,960	Medium	⊥	CH_2
2,930	Medium	⊥	CH_3
2,860	Shoulder	—	CH_2
1,730	Strong	‖	C=O
975	Medium	⊥	—

Assignment	Frequency (cm^{-1})	Intensity	Polarization
CH_3 rock and C−C skeletal	973	Medium	⊥
C−O stretch and others	1,053	Strong	—
C−O stretch and C−C skeletal	1,130	Medium-strong	—
C−O stretch and C−C skeletal	1,181	Strong	—
C−C−O stretch	1,276	Strong	—
CH_3 symmetric deformation (umbrella)	1,378	Medium	—
CH_2 deformation, CH3 asymmetric deformation	1,454	Medium	—
C=O stretch	1,726	Very strong	‖
CH_2 symmetric stretch	2,854	Medium	—
CH_2 asymmetric stretch	2,927	Medium	⊥
CH_3 asymmetric stretch	2,974	Weak	⊥

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
[1]H chemical shift	ppm	Solution state: 2.0 (w/v)% polymer solution in $CDCl_3$, 500 MHz (27°C). Bacterial product (strain: *B. megaterium*)		(9)
		d, CH_3	1.27	
		m, CH	5.26	
		m, CH_2	2.45–2.65	
Spin–spin coupling constant H_A CH_{X_3} —C—C——C—O— O H_B H_M	Hz	Solution state: 2.0 (w/v)% polymer solution in $CDCl_3$, 500 MHz (27°C). Bacterial product (strain: *B. megaterium)*		(9)
		J_{AB}	−15.5	
		J_{AM}	5.7	
		J_{BM}	7.3	
		J_{MX}	6.4	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
^{13}C chemical shift	ppm	Bacterial product (strain: *A. eutrophus*, 100% isotactic). Solution state: 2.0 (w/v)% polymer solution in $CDCl_3$, 125.7 MHz (27°C).		(10)
		CH_3	19.8	
		CH_2	40.8	
		CH	67.6	
		C=O	169.2	
		Solid state: CP/DD/MAS 67.8 Hz		(10)
		CH_3	21.3	
		CH_2	42.8	
		CH	68.4	
		C=O	169.8	
		Solution state: 3–5 (w/v)% polymer solution in $CDCl_3$, 125 MHz (room temperature)		(11)
		Isotactic (88% dyad), C=O	169.10	
		Syndiotactic (66% dyad), C=O	169.09, 169.11, 169.20, 169.22	
		Solid state: CP/MAS, 75.3 MHz		(12)
		Isotactic		
		CH_3	21.3	
		CH_2	42.9	
		CH	68.5	
		C=O	170.2	
		Syndiotactic		
		CH_3	20.4	
		CH_2	40.7	
		CH	68.7	
		C=O	170.7	
Common solvents	–	Soluble in:		
		Chloroform, trichloroethylene, 2,2,2-trifluoroethanol, dimethylformamide, ethylacetoacetate, triolein, comphor, glacial acetic acid, 0.5 N aqueous phenol, N-NaOH, *N*-hyamine hydroxide (NH_4OH)		(13)
		Methylene chloride		(14)
		1,1,2,2-Tetrachloroethane		(15)
		Triacetin (glycerol triacetate) (110°C)		(16)
		Dichloroacetic acid		(17)
		Propylene carbonate, 1,2-dichloroethane		(4)
		Partially soluble in:		
		Dioxane, toluene, octanol, pyridine		(13)
		Benzene, xylene, aniline, oleic acid dibutyphthalate		(18)
Nonsolvents	–	*n*-Hexane, carbon tetrachloride, acetone*, ethyl acetate, ether, methanol, ethanol, water, dilute mineral acid, alkaline hypochlorite		(13)
		Isopropanol, *n*-butanol, methylal, glycerides		(18)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Solubility parameter	$(MPa)^{1/2}$	Calculated using Hoy's group contributions of molar attraction constant	19.2	(19)
Solubility parameter of solvent	$(MPa)^{1/2}$	Soluble in:		(20)
		Chloroform	19.0	
		Trichloroethylene	18.8	
		2,2,2-Trifluoroethanol[†]	22.2	
		Dimethylformamide	24.8	
		Ethylacetoacetate	17.7	
		Triolein[†]	18.5	
		Camphor[†]	15.2	
		Glacial acetic acid	20.7	
		Methylene chloride	19.8	
		1,1,2,2-Tetrachloroethane	19.8	
		Triacetin[†]	19.4	
		Dichloroacetic acid	22.5	
		Propylene carbonate	27.2	
		1,2-Dichloroethane	20.1	
		Partially soluble in:		(20)
		Dioxane	20.5	
		Toluene	18.2	
		Octanol	21.1	
		Pyridine	21.9	
		Benzene	18.8	
		Xylene	18.0	
		Aniline	21.1	
		Oleic acid[†]	17.2	
		Dibutylphthalate	19.0	
Solubility parameter of nonsolvent	$(MPa)^{1/2}$	*n*-Hexane	14.9	(20)
		Carbon tetrachloride	17.6	
		Acetone	20.3	
		Ethyl Acetate	18.6	
		Diethyl ether	15.1	
		Methanol	29.7	
		Ethanol	26.0	
		Isopropanol	23.5	
		n-Butanol	23.3	
		Methylal[†]	17.4	
Interaction parameter χ	—	Chloroform, 30°C, $M_n = 127,000$	0.361	(21)

[*]Acetone is a solvent for amorphous PHB.

[†]Solubility parameters calculated from Klevelen and Hoftyzer's group contributions of solubility parameter components in reference (19).

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Second virial coefficient A_2

	Light scattering in trifluoroethanol, 25°C	Osmotic pressure in chloroform, 35°C	
$M_n \times 10^{-4}$	$A_2 \times 10^4$ (mol cm^3 g^{-2})	$A_2 \times 10^4$ (mol cm^3 g^{-2})	Reference
910 ± 20	6.20 ± 0.2	–	(22)
761 ± 30	6.28 ± 0.2	–	(22)
667 ± 20	6.38 ± 0.2	–	(22)
590 ± 10	6.52 ± 0.2	–	(22)
380 ± 10	6.88 ± 0.2	–	(22)
335 ± 5	7.12 ± 0.2	–	(22)
252 ± 5	8.06 ± 0.2	–	(22)
183 ± 2	8.24 ± 0.2	–	(22)
120 ± 1	9.56 ± 0.1	–	(22)
77.9 ± 1	10.2 ± 0.1	–	(22)
63.0	10.6	6.07	(5)
53.3	10.6	8.40	(5)
37.4	12.4	8.72	(5)
23.6	13.5	9.34	(5)
22.9	12.9	10.3	(5)
11.5	16.4	12.5	(5)

Mark-Houwink-Sakurada parameters $[\eta] = K\,(M_w)^a$

Solvent	Temp. (°C)	$K \times 10^3$ (ml g^{-1})	a	Reference
Chloroform	30	7.7	0.82	(17)
	30	11.8	0.78	(5)
	30	16.6	0.76	(5)
Trifluoroethanol	30	25.1	0.74	(23)
	25	12.5	0.80	(5)
	25	22.2	0.76	(24)
	30	17.5	0.78	(24)
1,2-Dichloroethane	30	9.18	0.78	(5)
	30	16.8	0.74	(24)
n-Butyl chloride	13 (θ)	100	0.5	(24)
1-Chloronaphthalene	40	39.6	0.62	(24)

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Huggins constant k'	—	Solvent	Temp. (°C)	M_n		
		Chloroform	30	138,000	0.42	(17)
		Chloroform	30	127,000	0.35	(17)
		Chloroform	30	85,000	0.49	(17)
		Chloroform	30	66,000	0.65	(17)
		Chloroform	30	36,000	0.35	(17)
		Chloroform	30	31,700	0.44	(17)
		Chloroform	30	31,360	0.50	(17)
		Chloroform	30	20,400	0.63	(17)
		Chloroform-*d*	—	400,000	0.478	(15)
		Tetrachloro-ethane-*d*	—	400,000	1.72	(15)
Radius of gyration $\langle S^2\rangle^{1/2}$	Å	Light scattering, trifluoroethanol, 25°C				(22)
		$M_w \times 10^{-4}$				
		910 ± 20			$2{,}560 \pm 50$	
		761 ± 30			$2{,}320 \pm 50$	
		667 ± 20			$2{,}140 \pm 50$	
		590 ± 10			$1{,}980 \pm 20$	
		434 ± 20			$1{,}710 \pm 50$	
		380 ± 10			$1{,}490 \pm 20$	
		335 ± 5			$1{,}387 \pm 20$	
		252 ± 5			$1{,}191 \pm 20$	
		183 ± 2			952 ± 15	
		120 ± 1			769 ± 5	
		77.9 ± 1			586 ± 10	
		51.0 ± 0.5			431 ± 5	
Flory viscosity constant Φ	10^{-21} mol^{-1}	Calculated data from M_w, [η], and $\langle S^2\rangle$				(5)
		$M_w \times 10^{-4}$				
		339			1.95	
		164			1.94	
		135			1.80	
		85.7			2.24	
		63.0			2.01	
		53.3			2.18	
		37.4			2.10	
		23.6			1.99	
		22.9			1.74	
		11.5			1.61	
Intrinsic sedimentation S°	10^{-13} s^{-1}	M_w				(17)
		780,000			−9.95	
		370,000			−8.16	
		156,000			−4.96	
		83,500			−3.50	
		21,100			−2.00	

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Degree of crystallinity	%	Purification	Drying	Annealing		
		Enzyme	Spray-dry	None	70	(25)
		Enzyme	Spray-dry	120°C, 48 h	80	(25)
		Hypochlorite	Freeze-dry	None	30	(25)
		Solution precipitation	Vacuum	160°C, 24 h	86	(26)
Lattice	–	Isotactic, α form			Orthorhombic	(8)
Space group	–	Isotactic, α form			$P2_12_12_1$	(8)

	Cell dimension (A)			Packing energy (Kcal mol^{-1})*			Torsional angle summary				
Form	*a*	*b*	*c*	v. der W.	C.E.	Total	$-[CH(CH_3)-CH_2-C(O)-O]_n-$				Reference
α	5.76	13.20	5.96	−28.7	−13.5	−42.2	142	−57	−31	180	(27)
α	5.76	13.20	5.96	−28.5	−14.7	−43.2	152	−52	−42	−175	(28)
α	5.73	13.14	5.93	−29.1	−47.4	−76.5	149	−59	−35	−173	(29)
β	–	–	4.6	–	–	–	112	−179	−110	174	(30)

*Packing energies calculated in a Dreiding II force field (Cerius^2 from Molecular Simulation, Inc.)

PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Heat of fusion ΔH	kJ mol^{-1}	86% crystallinity, DSC (differential scanning calorimetry)		12.5	(26)
Density	g cm^{-3}	Amorphous (extrapolation data from specific volumes)		1.177	(26)
		Crystalline (calculated data from crystal lattice parameters)		1.262	(8)
		Sample	Pretreatment		
		Film	None	1.232	(21)
		Film	Hot-stretched	1.250	(21)
Glass transition temperature T_g	K	Amorphous PHB			
		Dilatometry		269–274	(26)
		Dynamic mechanical measurement		268–278	(26)
		3 mol% 3HV		281	(31)
		9 mol% 3HV		279	(31)
		14 mol% 3HV		277	(31)
		20 mol% 3HV		272	(31)
		25 mol% 3HV		267	(31)

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Melting temperature T_m (optical observation)		3 mol% 3HV		443	(31)
		9 mol% 3HV		435	
		14 mol% 3HV		423	
		20 mol% 3HV		418	
		25 mol% 3HV		410	
		M_n	Method		(32)
		85,500	Osmotic pressure	453	
		52,400	Osmotic pressure	453	
		42,000	Osmotic pressure	447	
		31,360	Osmotic pressure	444	
		20,400	Osmotic pressure	443	
		15,100	Osmotic pressure	438	
		4,970	Osmotic pressure	419	
		1,870	Osmotic pressure	387	
		688	Chromatography	374	
		602	Chromatography	362	
		516	Chromatography	354	
		430	Chromatography	338	
		344	Chromatography	320	
Equilibrium melting point of infinite crystal T_m°	K	Calculated data from fitting of crystalline growth rate to Hoffman's theory		470 ± 2	(26)
Tensile modulus	MPa	–		1,400–2,200	(33)
Tensile strength	MPa	–		40	(31, 34, 35)
		Cold-rolling treatment		60	(33)
		10 mol% 3HV		25	(36)
		20 mol% 3HV		20	(36)
Flexural modulus	MPa	–		4,000	(35)
		–		3,500	(36)
		10 mol% 3HV		1,200	(36)
		20 mol% 3HV		800	(36)
Young's modulus	MPa	–		3,500	(31)
		Biaxially drawn film		4,000	
		3 mol% 3HV		2,900	
		9 mol% 3HV		1,900	
		14 mol% 3HV		1,500	
		20 mol% 3HV		1,200	
		25 mol% 3HV		700	
Extension at break	%	–		6	(31, 35)
		–		$6 \sim 8$	(34)
		–		8	(36)
		Biaxially drawn film		75	(31)
		10 mol% 3HV		20	(36)
		20 mol% 3HV		50	(36)

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Stress at break	MPa	Biaxially drawn film		100	(31)
Breaking strain	%	Cold-rolling treatment		130	(33)
Notched Izod impact strength	$J\,m^{-1}$	—		35	(37)
		—		50	(31)
		3 mol% 3HV		60	(31)
		9 mol% 3HV		95	(31)
		14 mol% 3HV		120	(31)
		20 mol% 3HV		200	(31)
		25 mol% 3HV		400	(31)
Solvent resistance	—	—		Poor	(34, 35)
UV resistance	—	—		Good	(34, 35)
Fold surface free energy σ_e	$mJ\,m^{-2}$	Calculated data from plot of T_m as function of inverse lamellar thickness		38 ± 6	(26)
Specific rotation $[\alpha]^{30}$	Degree	Solvent	λ (nm)		
		Chloroform (room temp.)	350	11	(38)
			589	−2	(38)
		Ethylene dichloride (at 25°C)	350	21	(5)
			589	0	(5)
		Dimethyl formamide (at 60°C)	350	16	(5)
			589	−3	(5)
		Trifluoroethanol	350	28	(5)
			589	0	(5)
		Dichloroacetic acid	350	80	(5)
			589	14	(5)
		2-Chloroethanol	350	33	(5)
			589	2	(5)
Oxygen permeability coefficient	m^3 (STP) $m\,s^{-1}\,m^{-2}\,Pa^{-1}$			2.1	(31, 34)

Pyrolysis[39]

Degradation temperature (°C)	$M_n \times 10^{-3}$ (M_w/M_n)						Rate constant (k_d)
	0 min.	1 min.	2 min.	5 min.	10 min.	20 min.	
175	546 (2.1)	505 (2.2)	417 (2.2)	—	—	146 (1.9)	$2.2 \pm 0.5 \times 10^{-5}$
180	477 (2.2)	432 (2.0)	434 (1.8)	312 (2.0)	169 (2.0)	93 (2.1)	$3.8 \pm 0.1 \times 10^{-5}$
190	402 (2.1)	192 (2.9)	136 (3.3)	—	52 (2.4)	—	$1.4 \pm 0.1 \times 10^{-4}$
200	282 (2.0)	121 (2.2)	121 (2.2)	37 (2.4)	—	7 (3.9)	$6.2 \pm 0.5 \times 10^{-4}$

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Activation energy of random chain session	$kJ\,mol^{-1}$	Calculated from Arrhenius plot for rate constant k_d. Temperature range: 170–200°C	212 ± 10	(39)
Biodegradability of PHB single crystals		Sample films incubated with *P. lemoignei* and *A. fumigatus* extracellular depolymerase		(40)

Sample (% isotactic dyads)	M_w ($g\,ml^{-1}$)	Heat of fusion ($J\,g^{-1}$)	Degradation time (h)	Weight loss (%)
100	500,000	85	50	100
79	130,000	51	890	64
55	9,500	14	730	84
34	2,700	30	890	45

Biodegradation* (41)

Environment	Temperature (°C)	Degradation time (weeks)
Sea water	15	350
Soil	25	75
Aerobic sewage	—	60
Anaerobic sewage	—	6

*All 1-mm thick samples.

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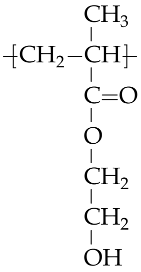
Poly(2-hydroxyethyl methacrylate)

NICHOLAS A. PEPPAS

ACRONYM, TRADE NAME PHEMA, Hydron

CLASS Vinylidene polymers

STRUCTURE



MAJOR APPLICATIONS Contact lenses, drug delivery systems, biomedical applications, chromatographic columns, flocculating agents.

PROPERTIES OF SPECIAL INTEREST Hydrophilicity. Good swelling in water and electrolytic solutions.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature	K	Isotactic	308	(1)
		Atactic	328	(2)
		Atactic	359	(3)
		Atactic	363	(4)
		Atactic	371	(5)
		Atactic	373	(6)
		Syndiotactic	382	(1)
		As a function of cross-linking ratio	388–399	(7)
Polymer-water interaction parameter χ_1	–	–	$0.32 + 0.904\upsilon_2$	(8)
			0.77–0.83	(9)
Water equilibrium volume fraction υ_2	–	Swelling	0.40	(2, 10)
			0.421	(11)
			0.395–0.431	(12, 13)
Water diffusion coefficient	$cm^2\,s^{-1}$	Diffusion at 7°C	2.17×10^{-6}	(14)
		Diffusion at 23°C	3.46×10^{-6}	(14)
		Diffusion at 34°C	4.78×10^{-6}	(14)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Water self diffusion coefficient	$cm^2\ s^{-1}$	—	$0.59–5.37 \times 10^{-6}$	(15)
Ion diffusion coefficient	$cm^2\ s^{-1}$	KF at 37°C	1.04×10^{-6}	(16)
		KCl at 37°C	1.34×10^{-6}	
		KBr at 37°C	1.42×10^{-6}	
		KI at 37°C	1.56×10^{-6}	
		$KHCO_3$ at 37°C	8.1×10^{-7}	
		K_2O_4 at 37°C	4.1×10^{-7}	
		KNO_3 at 37°C	1.5×10^{-6}	
		K_2CO_3 at 37°C	8×10^{-7}	
Linear expansion coefficient α_g	K^{-1}	Solid	3.7×10^{-4}	(17)
Storage modulus G' (sheer)	MPa	From −20 to 160°C	1.03–2.01	(18)
Swelling rate $\dot{v}$	h^{-1}	As a function of 0–1 wt% cross-linking agent	7–13.3	(19)

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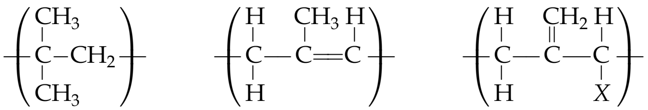
Poly(isobutylene), butyl rubber, halobutyl rubber

GARY W. VER STRATE AND DAVID J. LOHSE

ACRONYMS PIB, IIR (isobutylene isoprene rubber), ClIIR (chlorinated IIR), BrIIR (brominated IIR)[1,2]

CLASS Vinylidine polymers (IIR and halogenated derivatives are olefin-containing elastomers)

STRUCTURE[2]



PIB — IIR comonomer ~ 1% — Cl or Br IIR comonomer ~ 1% (X = Cl or Br)

PROPERTIES OF SPECIAL INTEREST High bulk density (0.917 g cm^{-3} at 20°C for PIB and IIR) for an amorphous elastomer, which leads to low gas permeability and high hysteresis at a given temperature. The introduction of a mole percent of olefin or halogen dramatically changes chemical reactivity but not physical properties.[2,3]

PREPARATIVE TECHNIQUES Type of polymerization: cationic, Lewis acids (e.g., $AlCl_3/H_2O$), −80°C[2,4]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Ceiling temperature	K	CO_2 at 139 bar	361	(5)
Typical comonomers	Isoprene, paramethyl styrene, halogen is introduced in a post polymerization process			(2)
Molecular weight (of repeat unit)	g mol^{-1}	Isobutene	56	(2)
Tacticity (stereoregularity)	Not applicable, backbone symetrically disubstituted. PIB will crystallize below 20°C or under stress (see below)			
Head-to-head contents	–	Negligible	–	(2, 6)
Degree of branching	Long chain branching is negligible except for intentionally branched commercially made products (e.g., Star branched butyl, Exxon Chemical)			(2)
Typical molecular weight range of polymer	g mol^{-1}	As dispersants, As elastomers In blends, viscosity modifiers, chewing gum	500–5,000 1–6 ($\times 10^5$) 5×10^3–6×10^6	(2)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Typical polydispersity index (M_w/M_n)	–	–	2.0–4.0	(2, 4)
IR (characteristic absorption frequencies)	cm^{-1}	Ambient, film, doublet	922; 948; also 1,225; 1,365; 1,385; 1,470	(7)
UV (characteristic absorption frequencies)	nm	Ambient, THF, hexane, broad centered at:	<200	(8)
NMR (compositional analysis)	^{13}C and ^{1}H NMR (see reference for detailed peak assignments)			(9–11)
Thermal expansion coefficients	K^{-1}	1 atm, 27°C $(1/V)(dV/dT)_P$	5.5×10^{-4}	(12)
Compressibility coefficients	bar^{-1}	$(1/V)(dV/dP)_T$	4.8×10^{9}	(12)
Reducing temperature T^*	K	150–250°C, 10–200 MPa	7,693	(12)
Reducing pressure P^*	$J\,cm^{-3}$	150–250°C, 10–200 MPa	469	(12)
Reducing volume V^*	$cm^3\,g^{-1}$	150–250°C, 10–200 MPa	0.959	(12)
Density (amorphous)	$g\,cm^{-3}$	1 atm, no halogen	$0.917(1 - 30/M_n)$	(13)
Solvents	Aromatic and aliphatic hydrocarbons, lubricating oils, nonpolar oxygen containing liquids			(2, 14)
Nonsolvents	Polar compounds, organic acids, ketones, alcohols with low carbon number, methyl chloride			(2, 14)
Solubility parameter	$(MPa)^{1/2}$	1 atm, 20°C	16.5	(15)
Theta temperature Θ	K	Toluene Ethyl hexanoate Benzene	260 330 296	(14, 16) (14, 17) (14, 17–19)
Interaction parameter χ	–	Cyclohexane, 25°C	0.44	(20)
Second virial coefficient A_2	$mol\,cm^3\,g^{-2}$	Cyclohexane, 23°C	$(6.9 \times 10^3)M_w^{0.2}$	(19)
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None	Cyclohexane, 25°C) Benzene, 25°C	$K = 0.0135$, $a = 0.74$ $K = 0.10$, $a = 0.504$	(19)
Huggins constant k'	–	Cyclohexane, 25°C	$0.233M_w^{0.095}$	(19)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Characteristic ratio $\langle r^2 \rangle_0/nl^2$	–	SANS, bulk polymer Benzene, 24°C	6.9 6.6	(21) (14)
Space group	–	Orthorhombic	$P2_12_12_1$	(22)
Chain conformation (ρ_n of helix)	–	–	2*8/3	(22)
Unit cell dimensions	Å	20°C, 1 atm	$a = 6.94$ $b = 11.96$ $c = 18.63$	(22)
Number of repeat units	–	–	16	(22)
Heat of fusion	$cal\ g^{-1}$	At the melting temperature, 1 atm	52	(22)
Density (crystalline)	$g\ cm^{-3}$	1 atm, 20°C	0.964	(22)
Glass transition temperature	K	1 atm, DSC	202, 208	(2, 14, 23)
Melting point	K	1 atm, depends on annealing conditions	275 317	(2, 14) (22)
Mesomeric transition temperatures	None of significance			
Sub-T_g transition temperatures	None of significance, but see reference; T_g behavior is complex			(24)
Heat capacity, $C_p = (dH/dT)_P$	$kJ\ K^{-1}\ mol^{-1}$	1 atm, 27°C	0.110	(14, 25)
Deflection temperature	K	–	<210	–
Polymers with which miscible	Ethylene-butene copolymers from 52 to 78 wt% Butene, LCST from 25 to 120°C Head-to-head polypropylene, LCST = 180°C			(12)
Tensile modulus	MPa	Depends on compounding ingredients, temperature, strain rate	0.5–50	(26)
Bulk modulus	MPa	Depends on compounding ingredients, temperature, strain rate	2,000	(14)
Shear modulus	MPa	Depends on compounding ingredients, temperature, strain rate	0.3–20	(14, 26)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Storage modulus	MPa	Depends on compounding ingredients, temperature, strain rate	0.3	(14, 23, 27, 28)
Loss modulus, tan δ	–	1 atm, 20°C, 1 Hz, uncross-linked, high molecular weight	0.3	(14, 23)
Tensile strength	MPa	Depends on compounding ingredients, temperature, strain rate	0.5–50	(26)
Maximum extensibility $(L/L_0)_r$	–	Depends on compounding ingredients, temperature, strain rate	8	(26)
Hardness	Shore A	Depends on compounding ingredients, temperature, strain rate	5–100	(27, 28)
Poisson's ratio	–	20°C	0.49	(14)
Plateau modulus	MPa	75 and 250°C, high M	0.032	(23)
Entanglement molecular weight	g mol^{-1}	75 and 250°C	7,100	(23)
WLF parameters: C_1 and C_2	C_1 = None C_2 = K	Uncross-linked PIB	$C_1 = 7.5$ $C_2 = 190$	(23)
Index of refraction n	None	1 atm, 25°C, n_D	$1.5092–13.9/M_n$	(13)
Refractive index increment dn/dc	ml g^{-1}	1 atm, THF, 27°C	$0.115\ (1 - 22/M_n)$	(13)
Dielectric constant ε'	–	1 atm, 20°C, 1 kHz	2.4	(14, 29)
Dielectric loss ε''	–	1 atm 20°C, 1 kHz	0.003	(14, 29)
Segment anisotropy	10^{25} cm^3	Benzene, xylene	45–59	(14, 30)
Electronic conductivity	(ohm cm)$^{-1}$	20°C, gum vulcanizate	10^{-14}	(25, 31)
Resistivity	log R, ohms	20°C, depends on carbon black, all 0.2 volume fraction	1.6–11.0	(31, 32)
Stress-optical coefficient	–	Data for a range of conditions	–	(24, 27)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Surface tension	$mN\,m^{-1}$	1 atm, 20°C	33.6	(14)
		150°C	25.3	
Interfacial tension	$nM\,m^{-1}$	With PDMS, 20°C	4.0	(33)
		With PVA		(34)
		20°C	9.9	
		100°C	8.3	
Permeability coefficient	$\frac{[m^3][cm]}{[S][m^2][Pa]}$	H_2, 250°C	5.43×10^{-17}	(35, 36)
		He, 25°C	6.37×10^{-17}	
		N_2, 25°C	0.243×10^{-17}	
	–	Miscellaneous organic solvents	–	(37, 38)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	1 atm, 20°C, gum vulcanizate	0.13	(25, 39)
		50 phr carbon black	0.23	
Melt viscosity	poise	Newtonian, 25°C	$(4.3 \times 10^{7})[\eta]^{4.66}$	(23)
			$(4.7 \times 10^{-11})M^{3.43}$	
			$(2.14 \times 10^{4})[\eta]^{4.74}$	
		Newtonian, 175°C	$[\eta]$ in cyclohexane at 25°C	
Coefficient of sliding friction μ	–	20°C, compounded vulcanizate, sliding on emery paper at 10^{-1} to 10^{3} cm s^{-1}	1.6	(40)
Pyrolyzability, nature of product	Pure PIB is completely combustible			(41)
Biodegradability, effective microorganisms	Inert			
Maximum use temperature	Up to 150°C continuous service (see manufacturers for compounding information)			(41)
Decomposition temperature	50% volatile for 30 min at 320°C			(41)
Cross-linking, quantum yield	PIB or IIR cross-link very poorly with chemically generated radicals or with radiation, these processes are not used commercially for those rubbers but see Cl, Br IIR below			
Scission		25°C, γ radiation, PIB		
$G(s)$ factor	$mol\,J^{-1}$		6.2×10^{-5}	(42)
$G(x)$	events/100 eV adsorbed		4	(14)

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^{60}Co irradiation at 77 K	Radicals	Cross-linking	Scission	Gas	Reference
	$G(R)$	$G(x)$	$G(s)$	G(isobutene)	
PIB	2.3	0.0	3.7	0.62	(10)
ClIIR	4.3	3.6	1.7	0.03	(10)
BrIIR	3.7	3.7	0.44	0.03	(10)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Water absorption	ppm	Pure polymer, 20°C, total immersion, compounding increases	<200	(36)
Cost	US\$ kg^{-1}	–	2.2	–
Availability	–	–	ktons	–
Suppliers	–	–	Exxon; Bayer	–

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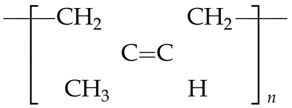
cis-1,4-Polyisoprene

RUZHI ZHANG

ACRONYMS, ALTERNATIVE NAMES, TRADE NAMES *cis*-PIP, CPI, IR, natural rubber (NR, NK), Hevea, *cis*-1,4-poly(2-methylbutadiene) (PMBD), Natsyn, Cariflex, Ebonite[1–3]

CLASS Diene elastomers

STRUCTURE



MAJOR APPLICATIONS *cis*-1,4-Polyisoprene is used in tires and tire products, foam rubber, rubber sheeting, rubber bands, hoses, gaskets, belts, molded and mechanical goods, footwear and sporting goods, gloves, sealants, adhesives, bottle nipple, caulking, and other typical elastomer applications.

PROPERTIES OF SPECIAL INTEREST High degree of stereoregularity in structure, presence of the reactive double bonds (unsaturation), strain-induced crystallization, high gum tensile strength, superior building tack, green stock strength, better processing, high strength in nonblack formulations, hot tear resistance, retention of strength at elevated temperatures, high resilience, low hysteresis (heat build-up), excellent dynamic properties, and general fatigue resistance.

NATURAL SOURCES Natural rubber occurs in over 200 species of plants. However, only one tree source, *Hevea Brasiliensis*, is of commercial importance, and it accounts for over 99 percent of the world's natural rubber production.[4–5]

PREPARATIVE METHODS *cis*-1,4-Polyisoprene is made by coordination, anionic, free-radical, or cationic polymerization of isoprene through the use of coordination catalysts, alkali metal catalysts, Alfin catalysts, organoalkani catalysts, or conventional Lewis acids.[6]

CHEMICAL MODIFICATION The following chemical modifications of *cis*-1,4-polyisoprene are employed as a convenient way of altering physical and mechanical properties: hydrohalogenation, halogenation, oxidation, ozonolysis, hydrogenation, carbene addition, cyclization.[6]

Typical composition (%) of natural rubber latex[7,8]

Total solid content	36
Dry rubber content	33
Proteineous substances	1–1.5
Resinous substances	1–2.5
Ash	< 1
Sugars	1
Water	60

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Physical constants of *cis*-1,4-polyisoprene (unvulcanized, CAS number [9003-31-0])

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	–	0.913	(9)
		0°C	0.9283	(10)
		20°C	0.9162	(10)
		Temp. range: 0–25°C, T in °C, densities as a function of temp. (measured above T_g)	$0.9283-6.10(\times 10^{-4})T$	(10)
Thermal expansion coefficients	K^{-1}	0°C	6.6×10^{-4}	(10)
		20°C	6.6×10^{-4}	
Tait equation parameters: C, b_0, and b_1	C = None	0–25°C, 0–500 bar, densities as a function of pressure	$C = 0.0894$	(10)
	b_0 = bar	0–25°C, 0–500 bar	$b_0 = 1{,}937$	
	$b_1 = °C^{-1}$	0–25°C, 0–500 bar	$b_1 = 0.00517$	
Isothemal compressibility	bar^{-1}	0°C, atmospheric pressure	4.6×10^{-5}	(10)
		20°C, atmospheric pressure	5.0×10^{-5}	
Thermal conductivity k	$W\,m^{-1}\,K^{-1}$	–	0.13	(9, 11, 12)
Specific heat C_p	$J\,kg^{-1}\,K^{-1}$	–	1.905×10^3	(13, 14)
$\partial C_p/\partial T$	$J\,kg^{-1}\,K^{-2}$	–	3.54	(13, 14)
Glass transition temperature	K	–	201	(15)
			199–204	(15, 16)
Melting point	K		308.6	(17, 18)
Heat of fusion ΔH_u	$kJ\,mol^{-1}$	Determined by use of diluent equation	4.393	(17, 18)
$\Delta H_u/M_o$	$J\,g^{-1}$	Determined by use of diluent equation	64.6	(17, 18)
Entropy of fusion ΔS_u	$J\,K^{-1}\,mol^{-1}$	Determined by use of diluent equation	14.2	(17, 18)
Heat of combustion	$kJ\,g^{-1}$	–	45.2	(9)
Temperature of most rapid crystallization	K	–	248	(19)
Refractive index n_D	–	–	1.5191	(20)
$\partial n_D/\partial T$	K^{-1}	–	−0.0037	(20)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric constant	—	1 kHz	2.37–2.45	(9, 21)
Dissipation factor	—	1 kHz	0.001–0.003	(21)
Conductivity	$S\,m^{-1}$	60 s	2.57×10^{-15}	(9, 21)
Bulk modulus	Pa	Isothermal K Adiabatic K_a	$1{,}940 \times 10^6$ $2{,}270 \times 10^6$	(10)
Bulk wave velocity V_b	$m\,s^{-1}$	Longitudinal wave	1,580	(10)
$\partial V_b/\partial T$	$m\,s^{-1}\,K^{-1}$	—	−3	(10)
Storage modulus G'	log Pa	Values of log G'	5.61 (5.53–5.75)	(22)
Loss modulus G''	log Pa	Values of log G''	4.46 (4.43–4.65)	(22)
Loss tangent G''/G'	—	—	0.09 (0.07–0.13)	(22)
Resilience	%	Rebound	75–77	(23, 24)
Unperturbed dimension $r_{0f}/M^{1/2}$	$nm\,mol^{1/2}\,g^{-1/2}$	Calculated unperturbed dimensions of freely rotating chains	$0.402/M_u^{1/2}$ $0.201/m^{1/2}$	(25)
Surface tension	$mN\,m^{-1}$	Contact angle	32	(26)

Physical constants of *cis*-1,4-polyisoprene (pure-gum vulcanizate)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	—	0.970	(27, 28)
		0°C	0.9211	(10)
		20°C	0.9093	(10)
		Temp. range: 0–25°C, T in °C, densities as a function of temp. (measured above T_g)	0.9210–5.86 $(\times 10^{-4})T$	(10)
Thermal expansion coefficients	K^{-1}	0°C	6.5×10^{-4}	(10)
		20°C	6.4×10^{-4}	(10)
		20°C	6.7×10^{-4}	(29)
Tait equation parameters: C, b_0, and b_1	C = None	0–25°C, 0–500 bar, densities as a function of pressure	C = 0.0894	(10)
	b_0 = bar	0–25°C, 0–500 bar	$b_0 = 1{,}916$	
	$b_1 = °C^{-1}$	0–25°C, 0–500 bar	$b_1 = 0.00425$	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Isothemal compressibility	bar^{-1}	0°C, atmospheric pressure	4.6×10^{-5}	(10)
		20°C, atmospheric pressure	5.0×10^{-5}	(10)
		20°C, atmospheric pressure	5.3×10^{-5}	(29)
Thermal conductivity k	$W\,m^{-1}\,K^{-1}$	–	0.153	(30, 31)
$(\partial k/k)/\partial T$	$\%\ K^{-1}$	–	0	(32)
			−0.1	(30)
Specific heat C_p	$J\,kg^{-1}\,K^{-1}$	–	1.828×10^{3}	(33)
Glass transition temperature	K	–	210	(34)
			201–212	
Melting point	K	–	313	(35)
Heat of combustion	$kJ\,g^{-1}$	–	44.4	(9)
Refractive index n_D	–	–	1.5264	(9)
$\partial n_D/\partial T$	K^{-1}	–	−0.0037	(9)
Dielectric constant	–	1 kHz	2.68	(21)
			2.5–3.0	(9, 21)
Dissipation factor	–	1 kHz	0.002–0.04	(21)
Conductivity	$S\,m^{-1}$	60 s	$2-100 \times 10^{-15}$	(9, 21)
Bulk modulus	Pa	Isothermal K	$1{,}950 \times 10^{6}$	(10)
		Adiabatic K_a	$2{,}260 \times 10^{6}$	
Bulk wave velocity V_b	$m\,s^{-1}$	Longitudinal wave	1,580	(10)
			1,500–1,580	(10, 36, 37)
$\partial V_b/\partial T$	$m\,s^{-1}\,K^{-1}$	–	−3	(10)
Strip velocity ν_1	$m\,s^{-1}$	Longitudinal wave, 1 kHz	45	(36)
			35–51	(9, 36, 38)
$\partial \nu_1/\partial T$	$m\,s^{-1}\,K^{-1}$	–	−0.2	(9)
Ultimate elongation	%	–	750–850	(23, 39)
Tensile strength	MPa	–	17–25	(23, 39)
Initial slope of stress-strain curve, Young's modulus, E	MPa	60 s	1.3	(40, 41)
			1.0–2.0	(23, 34, 40, 41)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Shear modulus G	MPa	60 s	0.43 0.3–0.7	(34, 41) (34, 42)
Shear compliance J	$(MPa)^{-1}$	60 s	2.3 1.5–3.5	(34, 41) (34, 42)
Creep rate $(1/J)(\partial J/\partial \log t)$	$\%(\text{unit} \log t)^{-1}$	–	2 1–3	(34, 40) (34, 40, 41, 43–45)
Poisson's ratio μ	–	Calculated as $0.5 - (1/6)(E/K)$	0.49989	(10, 46, 47)
E/G	–	Calculated as $3 - (1/3)(E/K)$	2.9978	(10, 46, 47)
Storage modulus G'	log Pa	Values of log G'	5.61 (5.49–5.78)	(48)
Loss modulus G''	log Pa	Values of log G''	3.80 (3.72–4.48)	(48)
Loss tangent G''/G'	–	–	0.016 (0.01–0.05)	(48)
Resilience	%	Rebound	75–84	(24, 49)

Unit cell dimensions

Lattice	Space group	Monomers per unit cell	Cell dimension (Å)			Cell angles	Reference
			a	*b*	*c*	γ	
Mono	C_{2h}^5	8	12.46	8.89	8.10	92°	(50)
Ortho	–	16	8.97	8.20	25.2	–	(51)
Mono	D_{2h}^{15}	16	26.3	8.15	8.9	109.5°	(52)
Ortho	–	8	12.4	8.15	8.9	–	(52, 53)

Permeability and diffusion data of *cis*-1,4-polyisoprene

Permeant	T (°C)	$P \times 10^{13}$	$D \times 10^6$	$S \times 10^6$	Temp. range (°C)	$P_o \times 10^7$	E_P	E_D	E_S	Reference
N_2	25	7.11	1.17	0.608	20–50	12.2	35.6	33.5	2.1	(54, 55)
CH_4	25	22.7	0.89	2.55	20–50	6.08	31.0	36.4	−5.4	(54)
C_2H_6	25	–	0.40	–	–	–	–	42.7	–	(54)
C_3H_6	25	154	0.31	49.7	20–50	17.7	28.9	42.7	−13.8	(54)
C_3H_8	25	126	0.21	60.0	20–50	1.34	23.0	46.5	−23.5	(54, 55)
SF_6	25	2.70	0.115	2.35	20–50	4.62	35.6	50.2	−14.6	(54)
C_2H_2	25	74.5	0.467	16.0	25–50	17.0	30.6	39.8	−9.2	(55)
n-C_4H_{10}	50	526	–	–	–	–	–	–	–	(56)
n-C_5H_{12}	50	1240	–	–	–	–	–	–	–	(56)
H_2O	25	1720	–	–	–	–	–	–	–	(57)

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Polymer pairs compatible in the amorphous state at room temperature (*cis*-1,4-polyisoprene is Polymer I)[58]

Polymer II	Method	Comments
Styrene	Single dynamic mechanical loss peak	I was natural rubber; II had $M_w \leq 350$; two peaks when II had $M_w \geq 600$
Vinyl cyclohexane	Single dynamic mechanical loss peak	I was natural rubber; II had $M_w \leq 375$; two peaks when II had $M_w \geq 650$

Infrared absorption[59–63]

Frequency (cm^{-1})	Assignment
836	Trisubstituted olefin out-of-plane CH wag*
1,129	CH_3rock
1,300	CH_2 wag
1,376	CH_3 symmetric (umbrella) deformation
1,450	CH_2 symmetric (scissors) and CH_3 asymmetric deformation
1,664	C=C stretch
2,720	Overtone of CH_2 umbrella
~2,850	CH_2 and CH_3 symmetric stretch
2,920	CH_2 asymmetric stretch
2,962	CH_3 asymmetric stretch
3,030	Olefin CH stretch

* Intensity increases with crystallinity.

Radiation resistance

Property	Half-value dose (MGy) in air at different dose rates (Gy h^{-1})					
	$\geq 10^5$	Reference	10^4	Reference	5	Reference
σ_R	3	(64)	>1	(65)	0.1	(65)
			1	(66)		
ε	1–1.5	(64)	>1	(65)	0.07	(65)
			1.5	(66)		

σ_R: Tensile strength at break (ultimate strength).
ε_R: Elongation at break (ultimate elongation).

Solvents and nonsolvents for *cis*-1,4-polyisoprene[67–69]

Solvents	Nonsolvents
Hydrocarbons, THF, higher ketones, higher aliphatic esters	Alcohol, lower ketones and esters, nitromethane, propionitrile, water, dilute acids, dilute alkalies, hypochlorite solutions

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Fractionation of *cis*-1,4-polyisoprene[70]

Method of fractionation	Solvent or solvent/nonsolvent mixture	Remarks
Fractional precipitation	Benzene/acetone	Havea
	Benzene/*n*-butanol	–
	Benzene/isopropanol	Low temperature
	Benzene/methanol	Low temperature
	Chloroform/acetone	Pale crepe
	Dichloroethane/2-butanone	–
	Toluene/*n*-butanol	30°C
	Toluene/boiling methanol	Chlorinated natural rubber
	Toluene/methanol	–
Fractional solution	Acetone	Havea, extraction
	Acetone, *n*-hexane	Guayule, extraction
	Benzene/methanol	25°C, column extraction, natural rubber
Chromatography	Benzene/methanol	Precipitation chromatography
	Chloroform	30°C, GPC, styragel
	Cyclohexane	GPC
	Cyclohexanone	Partition on paper
	o-Dichlorobenzene	GPC, 135°C
	Dichloromethane	GPC, μ-styragel
	Toluene	Preparative GPC, styragel
	Toluene/isopropyl alcohol	Precipitation chromatography

Solubility parameter

Polyisoprene	δ [(MPa)$^{1/2}$]	δ [(cal cm^{-3})$^{1/2}$]	Method	T (°C)	Reference
1,4-*cis*	15.18	7.42	Calculated	25	(71)
	20.46	10.0	Swelling	35	(72)
	16.57	8.10	Average	35	(72)
	16.47	8.05	Swelling	35	(72)
	16.68	8.15	Calculated	35	(72)
	16.68	8.15	Calculated	25	(73)
	16.2	7.9	Observed	25	(73)
	17.09	8.35	Observed	25	(73)
Natural rubber	17.0	8.3	Observed	25	(74)
	16.6	8.1	Observed	25	(75)
	17.09	8.35	Observed	25	(76)
	16.33	7.98	Observed	25	(77)
	16.49–16.42	8.06–8.12	Observed	25	(78)

Anisotropy of segments and monomer units of *cis*-1,4-polyisoprene

Solvent	$(\alpha_1 - \alpha_2) \times 10^{25}$ cm^3	$(\alpha_{\parallel} - \alpha_{\perp}) \times 10^{25}$ cm^3	Reference
Benzene	+48	+30.5	(79)
Squalene sw. p.	+53.1	–	(80)

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cis-1,4-Polyisoprene

Unperturbed dimensions of linear *cis*-1,4-polyisoprene

Property	Units	Value	Temp. (°C)	Remarks	Reference
$S_{0z}/M_w^{1/2} \times 10^4$	nm	0.76	22	Diisopropyl ether; 100% *cis*	(81)
$K_0 \times 10^3$	ml g^{-1}	130 ± 20	20	Benzene; 2-pentanone; 100% *cis*	(82, 83)
		119	14.5	2-Pentanone; 100% *cis*	(84)
		126	35	Cyclohexane; dioxane; 4-methyl-2-pentanone; toluene; 71% *cis*, 22% *trans*, 7% 3,4	(85)
$r_0/M^{1/2} \times 10^4$	nm	810 ± 45	20	Benzene; 2-pentanone; 100% *cis*	(82, 83)
		847	22	Diisopropyl ether; 100% *cis*	(81)
		766	35	Cyclohexane; dioxane; 4-methyl-2-pentanone; toluene; 71% *cis*, 22% *trans*, 7% 3,4	(85)
$r_{0f}/M^{1/2} \times 10^4$	nm	485	20	Benzene; 2-pentanone; 100% *cis*	(82, 83)
		485	22	Diisopropyl ether; 100% *cis*	(81)
$\sigma = r_0/r_{0f}$		1.67 ± 0.09	20	Benzene; 2-pentanone; 100% *cis*	(82, 83)
		1.74	22	Diisopropyl ether; 100% *cis*	(81)
$C_\infty = r_0^2/nl^2$		5.0	20	Benzene; 2-pentanone; 100% *cis*	(82, 83)
		5.5	22	Diisopropyl ether; 100% *cis*	(81)
		4.7	14.5	2-Pentanone; 100% *cis*	(84)
$d\ln r_0^2/dT$	Deg^{-1}	0.41×10^{-3}	$-10 \sim 70$	Undiluted; 100% *cis*	(84)
		0.56×10^{-3}	$30 \sim 70$	Undiluted; 100% *cis*	(84)

Mark-Houwink parameters: K and a (viscosity-molecular weight relationships, $[\eta] = KM^a$)

Polyisoprene	Solvent	T (°C)	$K \times 10^2$ (ml g^{-1})	a	Mol. wt. range $M \times 10^{-5}$	Method	Reference
Natural rubber	Benzene	30	1.85	0.74	0.8–2.8	OS	(83)
	Cyclohexane	27	3.0	0.70	18.5	LS, SD	(86)
	4-Methyl-2-pentanone	35	6.07	0.57	0.5–10	LS	(87)
	2-Pentanone	14.5	11.9	0.50	0.8–2.8	OS	(83)
	Toluene	25	5.02	0.667	0.7–10.0	OS	(88)
Synthetic *cis*	Hexane	20	6.84	0.58	0.5–8.0	SD	(89)
	Toluene	30	0.851	0.77	2.0–10.0	LS	(90)

Huggins coefficients for natural rubber[91]

Solvent	T (°C)	$[\eta]$	k'
Benzene	30	354	0.32
n-Hexane	30	170	0.35

Dipole moment of *cis*-1,4-polyisoprene in solution[92]

Solvent	T (°C)	P_n	$(\mu^2/N)^{1/2}$ (D)	φ	Remarks
Benzene	25.0	13,762	0.28	0.70	$u_o = 0.34D$ (2-methyl-2-butene in benzene)

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Heat of solution[93]

Solvent	Heat of solution ($J\ g^{-1}$ polymer)	Remarks
Benzene	12	16°C, $4 \times 10^3\ g\ mol^{-1}$

Second virial coefficient (A_2)

Polyisoprene	Solvent	Temp. (°C)	$M \times 10^{-6}$ ($g\ mol^{-1}$)	$A_2 \times 10^4$ ($mol\ cm^3\ g^{-2}$)	Reference
Cis	Cyclohexane	20	1.6	6.5	(94)
		25	0.62	5.0	(95)
Natural rubber		7	1.7	14.2	(86)
		27	1.7	14.3	(86)
		7	1.3	11.7	(96)
		27	1.3	12.7	(96)
		25	0.3	6.2	(95)

Sedimentation coefficients, diffusion coefficients, and frictional ratios for polyisoprene in solution

Polyisoprene	Solvent	Temp. (°C)	$M \times 10^{-3}$ ($g\ mol^{-1}$)	$s_o \times 10^{13}$ (s)	$D_o \times 10^7$ ($cm^2\ s$)	f_o/f_{sp}	Reference
Linear	Carbon tetrachloride	50	5	–	$D_o = 10^{-7.73\pm0.08} \times M^{-0.54\pm0.04}$	–	(97)
Natural rubber, crepe	Chloroform	20	270	15.5	2.24	3.32	(98)
			485	15.5	1.26	5.10	
			930	27.5	1.16	5.26	
			125	27.5	2.63	3.82	(98)
			275	27.5	1.64	4.71	
			450	27.5	1.41	4.64	
			760	27.5	1.44	3.82	
	Cyclohexane	20	1,600	4.6	0.48	3.82	
			1,750	4.76	0.46	3.82	
			1,800	4.35	0.41	3.82	
			1,600	4.6	0.48	3.82	(94)
Natural rubber	Hexane	20	270	9	3	3.82	(98)
			1,660	21	1.01	3.82	

Polymer-solvent interaction parameter χ

Solvent	Temp. (°C)	Volume fraction ϕ_2	χ	Reference
Acetone	0	1	2.1	(99)
	25	0.8–1	1.27–1.8	(99)
Benzene	10	0.6–0.8	0.42–0.43	(100)
	25	0–1	0.40–0.43	(100–102)
	25–55	1	0.46–0.43	(103)
	40	0.8–1	0.41–0.44	(100)
2-Butanone	25	0.6–1	0.86–1.43	(99)
	45	0.6–1	0.83–1.2	(99)

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Solvent	Temp. (°C)	Volume fraction ϕ_2	χ	Reference
Ethyl acetate	25	0.4–1	0.69–1.24	(99, 104)
	50	0.4–1	0.68–1.0	(99, 104)
Ethylbenzene	25–55	1	0.34–0.30	(103)
n-Heptane	25–55	1	0.51–0.49	(103)
n-Hexane	25–55	1	0.54–0.50	(103)
2-Methylheptane	25–55	1	0.50–0.47	(103)
2-Methylhexane	25–55	1	0.52–0.50	(103)
2-Methylpentane	25–55	1	0.56–0.52	(103)
n-Octane	25–55	1	0.49–0.46	(103)
n-Pentane	25–55	1	0.61–0.53	(103)
Toluene	25–55	1	0.36–0.32	(103)
2,2,4-Trimethylpentane	25–55	1	0.49–0.46	(103)
p-Xylene	25–55	1	0.28–0.26	(103)

Theta temperature

Polyisoprene	$M_w \times 10^{-4}$	Solvent	Theta temp. (°C)	$K_\theta \times 10^4$ [dl g^{-1}(g mol wt)$^{-1/2}$]	Reference
Cis	5–100	*n*-Hexane/isopropanol (50/50)	21.0	16.6	(105)
Cis (96%)	6.9–75	Dioxane	31.2	13.4	(106)
Cis (94%) linear	9.4	Methyl isobutyl ketone	16.5	—	(107)
	—	Methyl propyl ketone	33.0	—	(107)
3 branches	5.7 (Br: 1.75)	Methyl propyl ketone	33.0	—	(107)
11 branches	18 (Br: 1.6)	Methyl propyl ketone	27.8	—	(107)
22 branches	34.2 (Br: 1.6)	Methyl propyl ketone	23.5	—	(107)
		Methyl isobutyl ketone	15.0	—	(107)

Specific refractive index increment in dilute solution, dn/dc (ml g^{-1})

Polyisoprene	Solvent	$\lambda_0 = 436$ nm	$\lambda_0 = 546$ nm	T (°C)	Reference
Cis-1,4	Tetrahydrofuran	—	0.128	20	(108)
	Tetrahydrofuran	0.160 (calc.)	—	19–21	(109)
Chlorinated	Methyl ethyl ketone	0.131	—	35	(110)
Synthetic, high *cis*	Chloroform	0.104	0.100	25	(111)
Natural Hevea	Chloroform	0.106	0.104	25	(111)
Natural Guayule	Chloroform	0.108	0.101	25	(111)
	Cyclohexane	0.117	—	35	(112)
Synthetic, high *cis*	*n*-Hexane	0.192	0.191	25	(111)
Natural Hevea	*n*-Hexane	0.200	0.198	25	(111)
Natural Guayule	*n*-Hexane	0.198	0.193	25	(111)
Synthetic, high *cis*	THF	0.153	0.148	25	(111)
Natural Hevea	THF	0.160	0.156	25	(111)
Natural Guayule	THF	0.157	0.153	25	(111)
Synthetic	Toluene	0.030	0.028	25	(111)
Natural Hevea	Toluene	0.034	0.032	25	(111)
Natural Guayule	Toluene	0.033	0.030	25	(111)

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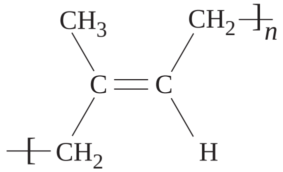
trans-1,4-Polyisoprene

GURU SANKAR RAJAN

ACRONYM, ALTERNATIVE NAMES, TRADE NAME[1–4] *trans*-PIP, gutta percha, balata, TP 301

CLASS Diene elastomers

STRUCTURE[1–5]



GENERAL INFORMATION Gutta percha from Malaysia (Palaquim gutta and Dichopsis gutta), balata from Brazil (Bolle tree); hard, crystalline thermoplastic material; synthetic *trans*-1,4-polyisoprene (TP 301: Kuraray Co., Ltd., Japan).[4,6]

MAJOR APPLICATIONS Used mainly in high-quality golf ball covers and orthopedic devices and splints; in transmission belts, cable coverings, and adhesives; and in prosthetics, braces, casts, and attachments for artificial limbs.[4,5]

PROPERTIES OF SPECIAL INTEREST The polymer resists abrasion, scuffing, and cutting; it is a tough, rigid, durable, and lightweight polymer at room temperature; it softens in hot water and does not crystallize immediately when cooled; it can be extruded, calendered, injection molded, and compression molded; it can be compounded with fillers and used in blends with other polymers; resistant to ozone, alkalies, fats, oils, and some concentrated acids except nitric acid and sulfuric acid.[4,5]

Preparative technique[4,7,8]

Catalysts	% *trans*-1,4
AlR_3 or $AlR_2Cl + VCl_3$	≥99
AlR_3 + supported VCl_3	≥98
AlR_3–VCl_3–$Ti(OR)_4$	≥99
Allylsodium-sodium isoperoxide-sodium chloride	52
Sodium or potassium metals in *n*-heptane	48–58
Polymerization	
Anionic: *sec*-C_4H_9Li (initiator), THF, 30°C	69 ± 2
Cationic: BF_3, $SnCl_4$, or $AlCl_3$ in pentane, chloroform, or ethylbenzene, −78 to 30°C	90%
Free-radical: water, isoprene, potassium fatty acid soap, potassium chloride, initiator-potassium persulfate, *tert*-dodecyl mercaptan, 50°C, 15 h	71.9%
Free-radical: initiator-cumene hydroperoxide, 5°C	86.2
In solution (alkali metals) or emulsion (free-radical)	

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PROPERTY	UNITS	CONDITIONS		VALUE		REFERENCE
Average molecular weight	$g\,mol^{-1}$	TP-301				(9)
		M_w		1.4×10^5		
		M_n		7.0×10^4		
Density	$g\,cm^{-3}$	TP-301		0.96		(4)
Mooney viscosity	—	ML 1 + 4, 100°C				(4)
		TP-301		30		
		Natural balata		25–33		
Melting temperature	K	TP-301		340		(4)
		Natural balata		340		(4)
		Synthetic		333		(10)
Glass transition temperature	K	Gutta percha		205		(11)
		Balata		204		(11)
		Synthetic		203		(11)
		Synthetic		213		(10)
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None		MW range ($M \times 10^{-4}$)	$K \times 10^3$	a	(12, 13)
		Synthetic *trans*, benzene, 32°C	8–140	43.7	0.65	
		Synthetic *trans* (98%), benzene, 30°C	14–77	18.1	0.72	
		Synthetic *trans* (98%), cyclohexane, 30°C	14–77	16.2	0.74	
		Synthetic *trans* (98%), hexane, 30°C	14–77	13.8	0.71	
		Synthetic *trans* (98%), toluene, 30°C	14–77	17.6	0.73	
		Gutta percha, benzene, 25°C	0.2–5	35.5	0.71	
		Gutta percha, dioxane, 47.7°C	0.2–5	191	0.50	
		Gutta percha, propyl acetate, 60°C	10–20	232	0.50	
Refractive index n	—	Gutta percha (β)		1.509		(14)
		Gutta percha (α)		1.514		
Specific refractive index increment dn/dc	$ml\,g^{-1}$	$\lambda_0 = 436\,nm$		0.117		(13)
Surface tension γ	$mN\,m^{-1}$	20°C, contact angle		31		(15)
Solubility parameter δ	$(MPa)^{1/2}$	Calculated		16.6		(15)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dipole moment per monomer unit $(\mu^2 N^{-1})^{1/2}$	D	Benzene, 25°C, number-average degree of polymerization = 3,125	0.31	(16)
Intrinsic segmental anisotropy $(\alpha_1 - \alpha_2) \times 10^{25}$	cm^3	Benzene	+49	(17)
Solvents	—	For gutta percha	Hot petroleum ether, benzene, chloroform	(18)
Nonsolvents	—	For gutta percha	Alcohol, water	(18)

Theta temperatures[19]

Solvent	Theta temp. (K)	$K_\theta \times 10^4$ (dl g−1 (g mol. wt.)$^{-1/2}$)
n-Propyl acetate*	333	—
Toluene/*i*-propanol		
(68.4/31.6)	298	22.2
(67.6/32.4)	303	21.9
(66.5/33.5)	308	21.7
(65.8/34.2)	313	21.4
(64.5/35.5)	318	21.3
(63.8/36.2)	323	21.1
Dioxane	320.7	19.1

*For gutta percha; rest of data for other 96% *trans*-polymer.

Unperturbed dimensions of 100% *trans*-polyisoprene*[20]

Solvent	$K_0 \times 10^3$ (ml g^{-1})	$r_0/M^{1/2} \times 10^4$ (nm)	$r_{0f}/M^{1/2} \times 10^4$ (nm)	$s = r_0/r_{0f}$	$C_\infty = r_0^2/nl^2$
Propyl acetate (60°C)	232	970	703	1.38	7.2
Dioxane (47.7°C)	191	910	703	1.30	6.35

*Calculated values of $r_{0f}/M^{1/2} \times 10^4$, nm mol$^{1/2}$ g$^{-1/2}$: $0.580/M_{u1/2}$ and $0.290/m_{1/2}$, where r_0 is the unperturbed root mean-square end-to-end distance, r_{0f} is the unperturbed root mean-square end-to-end distance of the freely-rotating chain, s is the effect of steric hindrance on the average chain dimension, C_∞ is the characteristic ratio, M_u is the molecular weight of the repeating unit, and m is the average molecular weight per skeletal link.

Crystallization constants for gutta percha[21]

Isothermal crystallization temperature T_c (K)	Half-time of crystallization $t_{1/2}$ (s)
308	768
313	1,260
318	6,780
320	11,700
322	19,800
326	64,500
330	291,000

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Growth kinetics coefficients[22]

trans-PIP	Fold surface free energy σ_e (J m^{-2})	Lateral surface free energy σ (J mol^{-1})	Work done by the chain to form a fold $\theta \times 10^{-5}$ (J mol^{-1})	Activation energy for polymer diffusion U^* (J mol^{-1})	Growth rate constant G_0 (cm s^{-1})	Nucleation rate constant $K_g \times 10^5$ (K^2)
A*	109×10^{-3}	—	0.31	6,280	1.10×10^3	2.17
B†	4.92×10^3 (J mol^{-1})	1,193	1.22	—	—	—

*$M_w = 170{,}000$; $T_g = -62.2$°C; $T_m^0 = 87$°C; $a_0 = 5.87$ Å; $b_0 = 3.95$ Å.
†$M_w = 390{,}000$; $T_m^0 = 74$°C; $M_n = 165{,}000$; $T_g = -59$°C.

Unit cell dimensions*[23]

Isomer	Lattice	Monomers per unit cell	Cell dimension (Å)		
			a	*b*	*c*
α form	Monoclinic, $P2_1/c$	4	7.98	6.29	8.77
β form	Orthorhombic, $P2_12_12_1$	4	7.78	11.78	4.72

*$\beta = 102°$.

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Poly(N-isopropyl acrylamide)

NICHOLAS A. PEPPAS

ACRONYMS PNIPA, PNIPAAm

CLASS Vinyl polymers

STRUCTURE $-[CH_2-CH]_n-$ with side chain $C{=}O$, NH, CH, CH_3 CH_3

MAJOR APPLICATIONS Membranes, chromatographic resins, size exclusion particles, drug delivery systems.

PROPERTIES OF SPECIAL INTEREST Exhibition of low critical solubility temperature in water at 32°C provides for interesting applications in separation science.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density, ρ	$g\,cm^{-3}$	Dry state	1.386	(1)
Polymer-water interaction parameter χ_1	–	Varying pressures, P (in MPa)	$0.505–1.39 \times 10^{-3}P$	(2)
		20°C	0.51	(1)
		40°C	0.95	(1)
		25°C	0.518	(3)
Lower critical solution temperature T_c	K	Hydrogels	303–308	(4)
		Aqueous solution	304	(5, 6)
Intrinsic viscosity $[\eta]$	$dL\,g^{-1}$	Aqueous solution at		(5)
		$T = 15$°C	2.74	
		$T = 25$°C	1.70	
		$T = 33$°C	1.44	
Mark–Houwink coefficient a	–	Solution in water at		(7)
		$T = 15$°C	0.93	
		$T = 25$°C	0.97	
		Solution in methanol at $T = 25$°C	0.64	
Refractive index n	–	Dry polymer	1.5	(8)
		Swollen polymer	1.36	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Storage modulus E' (compressive)	MPa	Polymer gel at		(9)
		$T = 30^{\circ}C$	0.1	
		$T = 60^{\circ}C$	1.3	
Loss modulus E'' (compressive)	MPa	Polymer gel at		(9)
		$T = 30^{\circ}C$	0.005	
		$T = 60^{\circ}C$	1.05	

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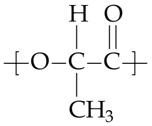
Poly(lactic acid)

LICHUN LU AND ANTONIOS G. MIKOS

ACRONYM PLA

CLASS Poly(α-hydroxy esters)

STRUCTURE



MAJOR APPLICATIONS L-PLA is used as sutures and dental, orthopedic, and drug delivery devices. D,L-PLA is used mainly for drug delivery. Both are of interest in the area of tissue engineering.

PROPERTIES OF SPECIAL INTEREST Good biocompatibility; biodegradable mainly by simple hydrolysis; bioresorbable; very good processability; a wide range of degradation rates, physical, mechanical, and other properties can be achieved by PLA of various molecular weights and its copolymers.

PREPARATIVE TECHNIQUES Practically useful high molecular weight PLA can be synthesized by a cationic ring opening polymerization of lactide using antimony, zinc, lead, or tin as catalyst and alcohol as molecular weight and reaction rate control agent at high temperature and low pressure.

IR of 1% w/v D,L-PLA in chloroform[1]

Structure	Absorption frequency (cm^{-1})
OH, alcohol and carboxylic acid	3,700–3,450
C=O	1,750–1,735
COO	1,600–1,580
C–O	1,200–1,000
CH	950–700

^{1}H NMR of 10% w/v D,L-PLA in deuteriochloroform[1]

Structure	Chemical shift (ppm) and peak multiplicity
OH	7.30, *s*
C$\underline{H}$–CH_3	5.20, *m*
CH–C$\underline{H}_3$	1.55, *d*

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^{13}C NMR of 10% w/v D,L-PLA in deuteriochloroform[1]

Structure	Chemical shift (ppm)
C=O	169.3
C–O	69.0
CH_3	16.7

Unit cell dimensions of L-PLA

Lattice	Monomers per unit cell	Cell dimension (Å)			Cell angles* γ (degree)	Chain conformation ρ_n of helix	Reference
		a	*b*	*c* (fiber axis)			
Hexagonal	—	5.9	5.9	—	120	—	(2)
Orthorhombic	—	10.31	18.21	9.00	90	3_1	(3)
Pseudo-orthorhombic	20	10.34	5.97	—	90	10_3	(2)
Pseudo-orthorhombic	20	10.6	6.1	28.8	90	10_3	(3)
Pseudo-orthorhombic	20	10.7	6.45	27.8	90	10_3	(4)

*Cell angles $\alpha = \beta = 90°$.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Degree of crystalline X_c	%	D-PLA	Semicrystalline	(5)
		L-PLA	0–37	(6)
		D,L-PLA	Amorphous	(6)
Density ρ	g cm^{-3}	P(L-co-DL)LA		(7)
		Amorphous	1.248	
		Single crystal	1.290	
Heat of fusion ΔH_f	kJ mol^{-1}	L-PLA complete crystalline	146	(8)
		L-PLA fiber		(9)
		As extruded	2.5	
		After hot-drawing	6.4	
Heat capacity C_p	J K^{-1} g^{-1}	L-PLA of		(10)
		$M_v = 5{,}300$	0.60	
		$M_v = (0.2–6.91) \times 10^5$	0.54	
Glass transition temperature T_g	K	L-PLA of various molecular weights	326–337	(5, 6, 8, 10, 11) (12)
		L-PLA with dichloromethane	—	(1, 5, 8)
		D,L-PLA of various molecular weights	323–330	(12)
		D,L-PLA with dichloromethane	—	
Melting point T_m	K	D-PLA injection-molded, $M_v = 21{,}000$	444.4	(13)
		L-PLA of various molecular weights	418–459	(5, 6, 8, 10, 11)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Equilibrium melting point	K	L-PLA of $M_v = 550{,}000$	488	(2)
		L-PLA	480	(14)
Secondary relaxation temperature	K	β-relaxation at 1 Hz (95% L-isomer)	228	(15)
Decomposition temperature T_d	K	L-PLA of $M_w = (0.5–3) \times 10^5$	508–528	(5)
		D,L-PLA of $M_w = (0.21–5.5) \times 10^5$	528	

Mark–Houwink parameters: K and a

Isoform	Solvent	Temp. (°C)	Conditions	$K \times 10^3$ (ml g^{-1})	a	Reference
Atactic	Benzene	30	For M_v	2.27	0.75	(16)
Atactic	Chloroform	25	For M_n	6.60	0.67	(1)
Atactic	Chloroform	25	For M_w	6.06	0.64	(1)
Atactic	Chloroform	25	For M_v	1.33	0.79	(12)
Atactic	Chloroform	30	For M_v	2.21	0.77	(16)
Atactic	Ethyl acetate	25	For M_n	1.58	0.78	(1)
Atactic	Ethyl acetate	25	For M_w	1.63	0.73	(1)
Isotactic	Benzene	30	For M_v	5.72	0.72	(16)
Isotactic	Chloroform	25	For M_v	2.48	0.77	(12)
Isotactic	Chloroform	30	For M_v	5.45	0.73	(16)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Solvents	Acetone at room temperature			(17)
	Benzene at $T = 30$°C			(16)
	Bromobenzene at $T = 85$°C			(18)
	Chloroform at $T = 25$°C			(12)
	m-Cresol at room temperature			(18)
	Dichloroacetic acid			(18)
	Dichloromethane at $T = 25$°C			(9)
	Dioxane at $T = 25$°C			(12)
	Dimethylformamide			(17)
	Ethyl acetate at $T = 25$°C			(1)
	Isoamyl alcohol			(2)
	N-methyl pyrrolidone			(12)
	Toluene			(19)
	Tetrahydrofuran			(1)
	Trichloromethane at $T = 25$°C			(9)
	p-Xylene			(2)
Equilibrium dissolution temperature	K	L-PLA in *p*-xylene	399.5	(2)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Cloud point temperature	K	D,L-PLA in dioxane/water mixture	–	(12)
Interaction parameter χ	–	L- or D,L-PLA in dioxane or chloroform at $T = 25°C$	0.1–0.3	(12)
Swelling	%	L- or D,L-PLA in methanol or water	–	(12)
		L-PLA film in 0.2 M pH 7 buffer	2	(6)
Second virial coefficient A_2	$mol\,cm^3\,g^{-2}$	L-PLA in bromobenzene at 85°C, $M_w = (0.8–4.9) \times 10^5$	$3.5–3.2 \times 10^{-4}$	(18)
Huggins constant	–	Atactic or isotactic in benzene	0.33–0.41	(16)
Steric hindrance parameter	–	Atactic in benzene or chloroform	1.98	(16)
		Isotactic in benzene or chloroform	2.69	
Characteristic ratio $\langle r^2 \rangle_0/nl^2$	–	L-PLA in bromobenzene at 85°C	2.0	(18)
Intrinsic viscosity $[\eta]$	$dl\,g^{-1}$	L-PLA		
		In chloroform at $T = 25°C$	3.8–8.2	(19)
		In chloroform at $T = 30°C$	2.63	(18)
		In bromobenzene at $T = 85°C$	1.38	(18)
		In chloroform	4.2	(12)
		In dioxane	3.2	(12)
		In N-methyl pyrrolidone	2.3	(12)
		L- or D,L-PLA in mixture of		
		Chloroform/methanol	–	(12)
		Dioxane/water	–	(12)
		D,L-PLA in chloroform at $T = 25°C$	0.1–1.5	(1)
Nucleation constant K_g	–	L-PLA crystallized from melt		
		Isothermal	2.44×10^5	(14)
		Nonisothermal	2.69×10^5	(20)
Fold surface energy σ_e	$J\,m^{-2}$	L-PLA crystallized from melt	60.89×10^{-3}	(14)
		L-PLA single crystals in *p*-xylene	75×10^{-3}	(2)
Lateral surface energy σ	$J\,m^{-2}$	L-PLA crystallized from melt		
		Isothermal	12.03×10^{-3}	(14)
		Nonisothermal	13.6×10^{-3}	(20)
Refractive index increment dn/dc	$ml\,g^{-1}$	L-PLA		
		In bromobenzene at $T = 85°C$	−0.06	(18)
		In tetrahydrofuran	0.0558	(21)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Optical rotation $[\alpha]_D$	Degrees	L-PLA at $T = 25°C$		
		In chloroform	−151	(18)
		In chloroform at $\lambda = 589$ nm	−161	(19)
		In dichloromethane	−162.8	(16)
		In chloroform/methanol mixture	−158 to −173	(12)
		In dioxane/water mixture	−165	(12)
		L-PLA in *p*-dioxane at $\lambda = 365$ nm	−443	(7)
Degradation rate	–	In vitro, L-PLA	–	(17, 22, 23)
		In vitro, D,L-PLA	–	(17)
		In vivo, D-PLA	–	(13)
		In vivo, L-PLA	–	(13, 17)
		In vivo, D,L-PLA	–	(13, 17)
		Mechanism	–	(24)

L-PLA ($[\eta] = 16\,cm^3\,g^{-1}$ in benzene at $T = 30°C$) under ^{60}Co radiation[25]

Atmosphere	Dose (M Gy)	Chain scission G factor	Cross-linking G factor
N_2	Low (<2.5)	26.5	4.5
N_2	Pregel region (>2.5)	40.5	11.0
Air	Low (<2.5)	14.5	0.4
Air	Pregel region (>2.5)	23.0	6.5

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength	MPa	L-PLA film or disk, $M_w = (0.5–3) \times 10^5$	28–50	(5)
		L-PLA melt-spun fiber	Up to 870	(26)
		L-PLA solution-spun fiber from		
		Toluene	Up to 1000	(19)
		Trichloromethane	Up to 1200	(9)
		Chloroform/toluene mixture	Up to 2300	(3)
		D,L-PLA film or disk, $M_w = (1.07–5.5) \times 10^5$	29–35	(5)
Tensile modulus	MPa	L-PLA film or disk, $M_w = (0.5–3) \times 10^5$	1,200–3,000	(5)
		L-PLA melt-spun fiber	Up to 9200	(26)
		L-PLA solution-spun fiber from		
		Toluene	Up to 10,000	(19)
		Trichloromethane	12,000–15,000	(9)
		Chloroform/toluene mixture	Up to 16,000	(3)
		D,L-PLA film or disk, $M_w = (1.07–5.5) \times 10^5$	1,900–2,400	(5)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile storage modulus E'	MPa	L-PLA varies with temperature		
		Melt-spun monofilament at 1 Hz	–	(27)
		Injection-molded bar at 3 Hz	–	(10)
		D,L-PLA varies with temperature		
		Film at 110 Hz	–	(8)
		Film at 11 Hz	–	(8)
Tensile loss modulus E''	MPa	L-PLA varies with temperature		
		Melt-spun monofilament at 1Hz	–	(27)
		Film or injection-molded bar at various frequencies	–	(10)
		D,L-PLA varies with temperature		
		Film at 110 Hz	–	(8)
		Film at 11 Hz	–	(8)
Flexural storage modulus	MPa	L-PLA film or disk $M_w = (0.5\text{–}3) \times 10^5$	1,400–3,250	(5)
		D,L-PLA film or disk, $M_w = (1.07\text{–}5.5) \times 10^5$	1,950–2,350	
Shear strength	MPa	L-PLA pin	54.5	(28)
Shear modulus	MPa	L-PLA melt-spun monofilament	1,210–1,430	(27)
Bending strength	MPa	L-PLA pin	132	(28)
Bending modulus	MPa	L-PLA pin	2,800	(28)
Elongation at yield	%	L-PLA film or disk, $M_w = (0.5\text{–}3) \times 10^5$	3.7–1.8	(5)
		D,L-PLA film or disk, $M_w = (1.07\text{–}5.5) \times 10^5$	4.0–3.5	(5)
Elongation at break	%	L-PLA film or disk, $M_w = (0.5\text{–}3) \times 10^5$	6.0–2.0	(5)
		L-PLA fiber spun from toluene	12–26	(19)
		L-PLA melt-spun fiber, $M_v = 1.8 \times 10^5$	25	(19)
		D,L-PLA film or disk, $M_w = (1.07\text{–}5.5) \times 10^5$	6.0–5.0	(5)

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Polymeric selenium

STEPHEN J. CLARSON

CLASS Inorganic and semi-inorganic polymers

STRUCTURE $-[\mathrm{Se}]_n-$

INTRODUCTION Selenium derives its name from the Greek name for the moon (selene)—in part due to its silvery appearance.[1] The most stable form of this element is gray selenium (metallic), which has a melting point of 494 K. This trigonal gray selenium consists of parallel spiral chains of Se atoms which repeat after three atoms. Red, crystalline selenium Se_8 rings (Se_{alpha} and Se_{beta}) can be obtained by crystallization from a carbon disulfide solution of black selenium. Black selenium is formed by pouring molten selenium in water. Detailed calculations on the conformations of polymeric selenium chains and on their ring-chain equilibration distributions have been described by Semlyen.[2,3] In the gas phase above the boiling point the dominant species is Se_2.

MAJOR APPLICATIONS Gray selenium has an electrical conductivity that increases with temperature and thus exhibits a semiconducting behavior. Selenium has also been demonstrated to be a photoconductor and hence finds applications as selenium photocells used for the measurement of the intensity of light.

PROPERTIES OF SPECIAL INTEREST Semiconductor and photoconductor.

Selected properties

PROPERTY	UNITS	CONDITIONS	VALUES	REFERENCE
Preparative techniques	—	—	—	(4)
Atomic number	—	—	34	—
Atomic mass	$g\,mol^{-1}$	—	78.96	—
Bond length	Å	l_{Se-Se}	2.34	(5)
Bond energy	$kJ\,mol^{-1}$	Se–Se Se=Se	172 290	(4)
Bond angle	Degrees	Se–Se–Se in Se_8 ring	106	(4)
van der Walls radius	Å	—	1.90	(5)
Melting point	K	Gray Se	494	(4)
Density	$g\,cm^{-3}$	220°C	4.06	(4)
Crystal structure	Å	Hexagonal	$a = 4.3640$ $c = 4.9594$	(4)

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PROPERTY	UNITS	CONDITIONS	VALUES	REFERENCE
Standard entropy of cyclization	cal deg^{-1} mol^{-1}	Polymeric selenium to cyclooctaselenium	−5.5	(4)
Enthalpy change	kcal mol^{-1}	For the formation of cyclooctaselenium	−2.3	(4)
Boiling point	K	Se	953	(4)

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Polymeric sulfur

STEPHEN J. CLARSON

CLASS Inorganic and semi-inorganic polymers

STRUCTURE $-[S]_n-$

INTRODUCTION Elemental sulfur has been studied throughout history—according to Kelly,[1] there are fifteen references to the element in the Bible. Sulfur is abundant in nature both in its elemental form and also as H_2S, SO_2, sulfide minerals, and various sulfates. It can exist as a large variety of allotropes, which depend on the temperature and pressure of the system. These consist of linear and cyclic $-[S]_n-$ species commonly from $n = 2$ to 20 for the rings and even much higher for the chains (species as long as 8×10^5 have been reported). The most stable form of sulfur at 25°C is the S_8 ring. When sulfur is poured onto ice water in the molten state plastic sulfur or catenasulfur is produced. Unlike the other sulfur allotropes, catenasulfur is insoluble in carbon disulfide (CS_2). Sulfur fibers can be produced that have helical conformations with approximately 3.5 S atoms per turn. Detailed calculations on the conformations of polymeric sulfur chains and on their ring-chain equilibration distributions have been described in a series of articles by Semlyen.[2–6]

MAJOR APPLICATIONS Although sulfur has many industrial applications in the area of organic and inorganic synthesis, in the field of polymer science and engineering it is probably best known for it use in the vulcanization of natural rubber and related unsaturated polymer chains (see Coran[7] and pertinent references cited therein). In this application, sulfur forms shorts chains, which link the polymer network precursor chains together by covalent bonding between the carbon containing chains at the sites of unsaturation. Another important area worth mentioning is the chemical reaction seen in proteins between two cysteine (S–H) units either on the same or on different chains to give covalent disulfide linkages (cystine units) (see Creighton[8] and pertinent references cited therein).

Selected properties

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Atomic number	–	–	16	–
Atomic mass	$g\,mol^1$	–	32.06	(9–11)
Bond length	Å	$l_{S–S}$	2.06 ± 0.02	(12)
Bond energy	$kJ\,mol^1$	S–S	265	(10)
Bond angle	Degrees	S–S–S in S_8 ring	108	(10)
van der Walls radius	Å	–	1.80	(12)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Standard entropy of cyclization	cal deg^{-1} mol^{-1}	Polymeric sulphur to cyclooctasulfur	−4.63	(12)
S_{alpha} (orthorhombic) to S_{beta} (monoclinic) transition temperature	K	–	368.5	(10)
Melting point	K	S_{alpha} S_{beta}	385.8 392	(10)
Boiling point S	K	–	717.6	(10)
$S_8 \rightarrow$ polymer critical polymerization temperature	K	–	432	(10)
Enthalpy $S_8 \rightarrow$ polymer	kJ mol^1	At 159°C	13.4	(10)
Temperature of maximum melt viscosity	K	–	~473	(10)

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Poly(methacrylic acid)

JIANYE WEN

ACRONYM PMAA, PMA

CLASS Vinylidene polymers

STRUCTURE

H CH_3
[—C—C—]
H COOH

MAJOR APPLICATIONS Various applications in the fields of mining, textile manufacture, cosmetics, oil recovery, agriculture, and water clarification as thickening agent for lattices and adhesives, ion-exchange resins, adhesives, binders, dispersants, and flocculating agents.

PROPERTIES OF SPECIAL INTEREST Weak acid, brittle solid that cannot be molded, cross-link on heating, decomposes without softening at high temperature, too water sensitive to be plastics, generation of viscosity and thixotropy at low concentrations, interaction with counter-ions or charged particulate matter, inverse solubility-temperature behavior.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	86.09	—
Density	$g\,cm^{-3}$	25°C	1.285	(1)
Glass-transition temperature T_g	K	—	403	(2)
			458	(3)
Heat capacity	$KJ\,K^{-1}\,mol^{-1}$	100 K	0.0452	(4)
		200 K	0.0814	
		300 K	0.1125	

Mark-Houwink parameters: *K* and *a*

Solvent	Temp. (°C)	Mol. wt. range ($M \times 10^{-4}$)	$K \times 10^3$ (ml g^{-1})	*a*	Reference
Methanol	26	−20	242	0.51	(5)
Aqueous HCl (0.002 M)	30	−90	66	0.50	(6)
Aqueous $NaNO_3$ (2 M)	25	−70	44.9	0.65	(7)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Properties of monomer				(8)
Melting point	K	–	287	
Boiling point	K	–	432–436	
Index of refraction	–	–	1.4288	
Specific gravity	–	–	1.015	
Heat capacity	$KJ\,K^{-1}\,mol^{-1}$	–	$(2.1–2.3) \times 10^{-3}$	
Dissociation constant pK	–	–	4.66	
Heat of polymerization	$kJ\,mol^{-1}$	–	56.5	
Solubility parameter	$(MPa)^{1/2}$	Isobutyl ester, 140°C	14.7	(9)
		Ethyl ester	18.31	(10)
		Methyl ester, 25°C	18.58	(11)
		Poor solvent hydrogen bonding	0	(12)
		Moderate	20.3	(12)
		Strong	26.0–29.7	(12)
Solvents	Ethanol, methanol, water, dioxane, dimethylformamide			(13)
	Alcohols, aqueous hydrogen chloride (0.002 M, above 30°C), dilute aqueous sodium hydroxide			(14, 15)
Nonsolvents	Acetone, diethyl ether, benzene, aliphatic hydrocarbons			(13)
	Ketones, carboxylic acids, esters			(14, 15)
Sound speed	$m\,s^{-1}$	Longitudinal	3,350	(1)

Tacticity[16,17]

Polymerization condition	Product
Free-radical polymerization in methyl ethyl ketone at 60°C	57% syndiotactic triads
Hydrolysis of poly(methacrylic anhydride) at 40°C	Atactic
Hydrolysis of esters having appropriate configurations	Syndiotactic

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Poly(methyl acrylate)

JIANYE WEN

ACRONYM PMA

CLASS Vinyl polymers

STRUCTURE $[-CH_2-CH(COOCH_3)-]$

MAJOR APPLICATIONS Coatings, textile finishing, paper saturants, and leather finishing.

PROPERTIES OF SPECIAL INTEREST A tough, rubbery, and moderately hard polymer with little or no tack at room temperature; superior resistance to degradation and remarkable retention of its original properties under use conditions.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	25°C	1.22	(1–3)
Glass transition temperature	K	–	279	(1, 4)
		Conventional	283, 284	(5–9)
		Head to tail	279	(10–14)
		Head to head	304	(15–20)
Heat capacity	$KJ\,K^{-1}\,mol^{-1}$	−173°C	0.0529	(21)
		−73°C	0.0844	
		27°C	0.1518	
		227°C	0.1843	
		ΔC_p	3.638/7.404	
Interaction parameter χ	–	Butane, 70–90°C	2.392–1.753	(22)
		Hexane, 70–110°C	2.731–1.885	(22)
		Heptane, 70–110°C	2.808–1.983	(22)
		Decane, 70–110°C	3.107–2.434	(22)
		Cyclohexane, 70–110°C	2.316–1.460	(22)
		Benzene, 70–110°C	0.471–0.359	(22)
		Toluene, 70–100°C	0.624–0.511	(22)
		Chloroform, 70–110°C	−0.222 to −0.075	(22)
		Carbon tetrachloride, 70–110°C	0.986–0.658	(22)
		Acetone, 70–110°C	0.482–0.384	(22)
		Methyl ethyl ketone, 70–110°C	0.459–0.388	(22)
		Tetrahydrofuran, 70–100°C	0.425–0.316	(22)
		Dioxane, 70–100°C	0.205–0.198	(22)
		Methyl acetate, 70–110°C	0.396–0.375	(22)
		Ethyl acetate, 70–110°C	0.471–0.428	(22)
		Butanone, 100°C	0.40	(23)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Interaction parameter χ	—	Ethanol, 100°C	1.01	(23)
		n-Octane, 90–100°C	2.4–2.2	(23, 24)
		1-Propanol, 100°C	0.82	(23)
Interfacial tension	$mN\,m^{-1}$	Poly(*n*-butyl acrylate), 20°C	4.0	(25)
		PE, 20°C	10.6	

Mark-Houwink parameters: *K* and *a*

Solvent	Temp. (°C)	Mol. wt. range ($M \times 10_4$)	$K \times 10_3$ ($ml\,g^{-1}$)	*a*	Reference
Acetone	25	−160	5.5	0.77	(26)
	30	−45	28.2	0.52	(26)
Benzene	25	−130	2.58	0.85	(26)
	30	−160	4.5	0.78	(26)
Butanone	20	−240	3.5	0.81	(26)
	25	−68	14.1	0.67	(27)
	30	−190	3.97	0.772	(28)
Diethyl malonate	30	−190	3.51	0.793	(28)
Ethyl acetate	35	−148	11	0.69	(29)
Toluene	30	−190	7.79	0.697	(28)
	35	−69	21	0.60	(29)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength	MPa	—	6.9	(30, 31)
Elongation at break	%	—	750	(30, 31)
Index of refraction n_{25}^{D}	—	—	1.479	(32)
Second virial coefficient A_2	10^4 ($mol\,cm^2\,g^{-2}$)	Acetone, 20°C, $M \times 10^{-3} = 77$–880	4.5–2.8	(33)
		Acetone, 25°C, $M \times 10^{-3} = 280$–2,500	4.2–2.4	(34, 35)
		Ethyl acetate, 35°C, $M \times 10^{-3} = 362$–1,480	1.92	(29)
		Butanone/isopropanol 58/42, 20°C, $M \times 10^{-3} = 290$–1,720	0.1–0.06	(34)
Solvents	Aromatic hydrocarbons, chlorinated hydrocarbons, tetrahydrofuran, esters, ketones, glycolic ester ethers, and phosphorus trichloride			(36)
Nonsolvents	Aliphatic hydrocarbons, hydrogenated naphthalenes, diethyl ether, alcohols, and carbon tetrachloride			(36)
Solubility parameter	$(MPa)^{1/2}$	1.479	20.7	(37)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Surface tension	$mN\,m^{-1}$	$M_w = 25{,}000$		(38)
		20°C	41.0	
		150°C	31.0	
		200°C	27.2	
	$mN\,m^{-1}\ K^{-1}$	$-d\gamma/dT$	0.070	
	χ^p	Polarity	0.248	

Unperturbed dimension*

Conditions	$r_0/M^{1/2} \times 10^4$ (nm)	$r_{0f}/M^{1/2} \times 10^4$ (nm)	$\sigma = r_0/r_0^2$	$C_\infty = r_0^2/nl^2$	Reference
Various solvents, 30°C	680 ± 30	332	2.05 ± 0.10	8.4	(39)
Butanone/2-propanol, 42/58 vol., 20°C	680	332	2.05	8.4	(34, 35)
50/50 vol., 30°C	665	332	2.00	8.0	(28)
Undiluted, 60°C	$d \ln r_0^2/dT = -0.2 \times 10^{-3}$ [$\deg^{-1}$]				(40)

*See reference (32) for details.

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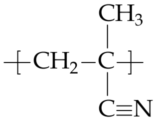
Poly(methacrylonitrile)

J. R. FRIED

ACRONYM PMAN

CLASS Polynitriles

STRUCTURE



MAJOR APPLICATIONS Films, coatings, elastomers, packaging, photoresists.

PROPERTIES OF SPECIAL INTEREST Good resistance to many solvents, acids, and water, but attacked by polar solvents and decomposed by concentrated alkali and hot dilute alkali.

TYPES OF POLYMERIZATION Free-radical or ionic polymerization of methacrylonitrile (2-cyanopropylene) in bulk, emulsion, or solution; group-transfer polymerization also has been used. Ionic polymerization in inert solvents can produce either amorphous poly(methacrylonitrile) (by use of anionic catalysts such as *n*-butyllithium) or primarily isotactic poly(methacrylonitrile) (by use of coordination catalysts such as ethylberyllium or diethylmagnesium).

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	67.09	–
Typical comonomers	Butadiene, styrene, *a*-methylstyrene, methacrylic acid			
Solvents	Trifluoroacetic acid, acetone, acetonitrile, acrylonitrile, aniline, benzaldehyde, *m*-cresol, cyclohexanone, N,N-dimethyl acetamide, N,N-dimethyl formamide, dimethyl sulfoxide, ethanol amine, formic acid, N-methyl-2-pyrolidone, nitrobenzene, propylene carbonate, pyridine, triethyl phosphate			(1)
Nonsolvents	Acetic acid, benzene, 1-butanone, *n*-butyl acetate, chlorobenzene, cyclohexane, diethyl ether, diethylene glycol, diisobutyl ketone, ethyl acetate, 2-ethyl hexanol, *n*-heptane, isoamyl alcohol, isopropyl alcohol, *n*-octyl alcohol, 1-propanol propylene glycol, styrene, tetralin, 1,1,1-trichloroethane, toluene			(1)
Ceiling temperature	K	In benzonitrile	418	(2)
Density	$g\,cm^{-3}$	Amorphous	1.13	(3)

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Poly(methacrylonitrile)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric constant ε' (D150)	—	60 Hz 1 kHz 1 MHz	4.14 3.83 3.30	(3)
Dissipation factor (D150)	—	60 Hz 1 kHz 1 MHz	0.046 0.038 0.025	(3)
Maximum extensibility $(L/L_0)_r$	%	D638	2–3	(3)
Flexural modulus	GPa	D790	3.86–4.48	(3)
Flexural strength	MPa	D790	83–97	(3)
Glass transition temperature	K	Amorphous (free-radical polymerization)	285	(4)
Hardness	M scale	Rockwell (D785)	95	(3)
Heat deflection temperature	K	D648 (1.8 MPa)	370–373	(3)
Impact strength	$J\,m^{-1}$	Notched Izod (D256)	21	(3)
Index of refraction n		At 20°C	1.5932	(3)
Solubility parameter	$(MPa)^{1/2}$	—	21.925.4	(5)(1)
Tensile strength	MPa	D638	55–69	(3)
Volume resistivity	ohm cm	—	1.14×10^{16}	(3)
Water absorption	%	144 h at ambient temperature	0.24	(3)
Infrared spectrum (principal absorptions)	cm^{-1}	Assignment CH_3 stretching C≡N stretching	Wavenumber 2,990 2,234.5	(6)
Permeability coefficient	m^3 (STP) $m\,s^{-1}\,m^{-2}\,Pa^{-1s}$	At 25°C O_2 CO_2 H_2O	 9×10^{-21} 2.4×10^{-20} 3.10×10^{-15}	(7)

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Unit cell dimensions[3]

Lattice	Monomers per unit cell	Cell dimension (Å)			Cell angles		
		a	*b*	*c**	α	β	γ
Pseudohexagonal (modification I)	—	9.03	—	6.87	—	—	—
Monoclinic (modification II)	8	13.5	7.71	7.62	—	97°49′	—

*Fiber identity period.

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Poly(N-methylcyclodisilazane)

DONNA M. NARSAVAGE-HEALD

ALTERNATIVE NAMES Poly(1,3-dimethyl-2,2,4,4-tetramethylcyclodisilazane); poly(hexamethylcyclodisilazane)

CLASS Polysilazanes

REPEAT UNIT $-[Me_2Si-NMe]-$

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Preparative techniques	–	Anionic ring opening		
		MeLi/THF	–	(1, 2)
		n-BuLi/THF		(1)
		n-BuLi/hexane		(2)
		t-BuLi/THF		(2)
		PhLi/THF		(1)
		MeLi/Me_3CONa/THF		(1)
		n-BuLi/Me_3CONa/THF		(1)
		Naphthalene-Na		(2)
		α-MeStyNa		(2)
		Cationic ring opening		
		CF_3SO_3Me		(2)
		$CF_3SO_3SiMe_3$		(2)
Molecular weight (of repeat unit)	$g\ mol^{-1}$	–	87	–
Molecular weight (M_n)	$g\ mol^{-1}$	MeLi/THF	3,000	(1)
		MeLi/THF	4,400	(2)
		n-BuLi/THF	1,500	(1)
		n-BuLi/hexane	1,020	(1)
		t-BuLi/THF	4,200	(2)
		PhLi/THF	4,200	(2)
		MeLi/Me_3CONa/THF	1,500	(1)
		Naphthalene-Na	16,000	(2)
		α-MeStyNa	4,000	(2)
		CF_3SO_3Me	16,800	(2)
		$CF_3SO_3SiMe_3$	18,000	(2)
Typical polydispersity index (M_w/M_n)	–	–	1.2	(2)
NMR	ppm	^{1}H	0.12 (SiMe), 2.39 (NMe)	(1, 2)
		^{13}C	1.94 (SiMe), 30.25 (NMe)	(1, 2)
		^{29}Si	−2.2	(1, 2)
		^{15}N	−361	(2)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature	K	DSC	235	(2)
Melting temperature	K	DSC	500	(2)
Phase transition	K	DSC	428	(2)
Pyrolyzability, amount of product	—	TGA, argon flow, 10°C min^{-1}	2.85%	(1)

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Poly(methylene oxide)

ALLAN S. HAY AND YONG DING

ALTERNATIVE NAMES, TRADE NAMES Polyacetal, polyoxymethylene, acetal, Delrin®, Celcon® (copolymer), Ultraform® (copolymer)

CLASS Polyether engineering thermoplastics

STRUCTURE $[-CH_2-O-]$

MAJOR APPLICATIONS Poly(methylene oxide) resin has been widely used in mechanical, automotive, plumbing, appliance, industrial, and electrical conponents along with its copolymer resins. It is continuing to replace die-cast zinc, brass, aluminum, steel, and other metals in the various end-use industries.

PROPERTIES OF SPECIAL INTEREST Poly(methylene oxide) resin, like other polyacetal resins, is a highly crystalline polymer characterized by its metallic qualities of hardness, strength, and stiffness. It also has good lubricity properties under a wide variety of enviromental conditions of moisture and heat, good fatigue resistance, a low coefficient of friction, and springiness. In addition, it has good chemical resistance to most solvents. It cannot, however, be flameproofed.

PREPARATIVE TECHNIQUES The homopolymer is prepared by anionic polymerization of purified formaldehyde with the addition of an initiator such as an amine, phosphine, or metal alcohol. The copolymers are manufactured commercially by copolymerization of trioxane, the cyclic trimer of formaldehyde, with small amounts of a comonomer. Typically, acetal copolymer reisns have 95% or more oxymethylene units.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight of repeat unit	$g\,mol^{-1}$	–	30.03	–
Typical molecular weight range of polymer	$g\,mol^{-1}$	–	2–9 × 104	–
IR (characteristic absorption frequencies)				(1, 2)
NMR				(3, 4)
Thermal expansion coefficients	K^{-1}	233–303 K	7.5×10^{-5}	(5)
Density (amorphous)	$g\,cm^{-3}$	D792		(6)
		Homopolymer	1.42	
		Copolymer	1.41	

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Solvents[5]

Solvent	Gel Temp. (K)	Dissolving Temp. (K)
m-Chlorophenol	328	362
Phenol	331	382
p-Chlorophenol	333	371
3,4-Xylenol	361	401
Aniline	375	403
γ-Butyrolactone	385	407
N,N-Dimethylformamide	388	408
Pentachloroethane	390	413
Ethylene carbonate	390	418
Benzyl alcohol	392	405
Styrene oxide	398	419
Formamide	403	423
Nitrobenzene	407	421
Cyclohexanol	413	423
Propionic anhydride	417	428

Mark-Houwink parameters: *K* and *a*

Solvent	Temp. (K)	$M_w \times 10^{-3}$ (g mol^{-1})	$K \times 102$ (ml g^{-1})	*a*	Reference
p-Chlorophenol	403	—	5.43	0.66	(7)
p-Chlorophenol, 2% α-pinene	333	62–129	4.13	0.724	(8)
1H,1H,5H-octafluoropentanol-1	383	62–129	1.33	0.81	(8)
Phenol-tetrachloroethane (25–75 wt.)/2% α-pinene	363	1.1–92	1.216	0.64	(9)
Phenol	363	—	1.13	0.76	(10)
Dimethylformamide	423	89–285	4.4	0.66	(11)
Dimethylformamide	403	1.5–15	2.24	0.71	(12)
Hexafluoroacetone-sesquihydrate + triethylamine	298	1.5–15	4.60	0.74	(12)

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Lattice	—	—	TRIG	ORTH	(13)
Space group	—	—	$P3_1$ or $P3_2$	$P2_12_12_1$	(13)
Chain conformation	—	—	2 * 9/5	2 * 2/1	(13)
Unit cell dimensions	Å	—	$a = 4.471$ $b = 4.471$ $c = 17.39$	$a = 4.767$ $b = 7.660$ $c = 3.563$	(13)
Unit cell contents (number of repeat units)			9	4	(13)
Density (crystalline)	g cm^{-3}	—	1.491	1.533	(13)

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Heat of fusion (of repeat units)	$kJ\,mol^{-1}$	–	9.79	–	(14)
Entropy of fusion (of repeat units)	$kJ\,K^{-1}\,mol^{-1}$	Constant pressure	8.21×10^{-3}		(15)
		Constant volume	4.98×10^{-3}		(15)
		Equilibrium value	10.70×10^{-3}		(16)
Degree of crystallinity	%	Homopolymer			
		293 K (density)	64–69		(17)
		298 K (x-ray)	77		(18)
		408 K (x-ray)	75		(18)
		413 K (x-ray)	73.0		(19)
		418 K (x-ray)	73.1		(19)
		423 K (x-ray)	75.4		(19)
		428 K (x-ray)	76.9		(19)
		430 K (x-ray)	67		(18)
		433 K (x-ray)	80.0		(19)
		440 K (x-ray)	95.5		(19)
		Copolymer, Hostaform C 2520, $M_w = 80{,}000$, 298 K (density)	56–59		(17)
		Copolymer, Hostaform C9020, $M_w = 58{,}000$, 298 K (density)	56.6		(17)
Glass transition temperature	K	–	198		(18)
Melting point	K	Delrin 500, ASTM D2133	448		(6)
		Celcon M90, ASTM D2133	438		
Heat capacity (of repeat units)	$J\,K^{-1}\,mol^{-1}$	Homopolymer			(20)
		0 K	0		
		50 K	9.94		
		100 K	16.69		
		200 K	28.82		
		300 K	42.79		
		Copolymer			(20)
		0 K	0		
		50 K	9.97		
		100 K	16.40		
		200 K	26.56		
		300 K	41.11		

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
		Crystalline polymer		(21)
		0 K	0	
		50 K	10.10	
		100 K	16.68	
		200 K	27.15	
		300 K	38.52	
Deflection temperature	K	Delrin 500		(6)
		ASTM D648, 1.82 Mpa	409	
		ASTM D648, 0.45 Mpa	445	
		Celcon M90		(6)
		ASTM D648, 1.82 Mpa	383	
		ASTM D648, 0.45 MPa	431	
Tensile modulus	MPa	296 K, ASTM D638		(5)
		Homopolymer	3,100	
		Copolymer	2,825	
Tensile strength	MPa	296 K, ASTM D638		(5)
		Homopolymer	68.9	
		Copolymer	60.6	
Maximum extensibility $(L/L_0)_r$	%	296 K, ASTM D638		(5)
		Homopolymer	23–75	
		Copolymer	40–75	
Flexural modulus	MPa	296 K, ASTM D790		(5)
		Homopolymer	2,830	
		Copolymer	2,584	
Flexural strength	MPa	296 K, ASTM D790		(5)
		Homopolymer	97.1	
		Copolymer	89.6	
Impact strength	J m-1	296 K, notched, 3.175 mm, ASTM D256		(5)
		Homopolymer	69–122	
		Copolymer	53–80	
		233 K, notched, 3.175 mm, ASTM D256		
		Homopolymer	53–95	
		Copolymer	43–64	
Hardness	–	Rockwell hardness, ASTM D785		(5)
		Homopolymer	94	
		Copolymer	80	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Shear stress	MPa	296 K, ASTM D732		(5)
		Homopolymer	65	
		Copolymer	53	
Dielectric constant ε'	–	102–106 Hz, ASTM D150		(5)
		Homopolymer	3.7	
		Copolymer	3.7	
Dielectric loss ε''	–	Copolymer, ASTM D150		(5)
		102 Hz	0.0010	
		103 Hz	0.0010	
		104 Hz	0.0015	
		106 Hz	0.006	

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Poly(methyl methacrylate)

SHAW LING HSU

ACRONYM, TRADE NAMES PMMA, Plexiglas, Lucite

CLASS Vinylidene polymers; acrylics

STRUCTURE $-[CH_2-C(CH_3)(COOCH_3)]-$

CHEMICAL REGISTRY NUMBER 9011-14-7

PROPERTIES OF SPECIAL INTEREST Optically clear (92% transmission, theoretical limit for normal incidence, in the visible region) through the visible wavelength range; very little ultraviolet absorption until 260 nm. Good mechanical properties. Extremely high weatherability. Commercial materials are usually atactic polymers (~75% syndiotactic), although isotactic and syndiotactic polymers have been synthesized. High sensitivity to electron radiation.

MAJOR APPLICATIONS Replacement for glass. Can be used as one-component-deep UV, electron-beam, or ion-beam resists in the manufacture of microelectronics chips.[1,2]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tacticity	Commercial grade materials generally have 50–70% syndiotactic, ~30% atactic, and <10% isotactic dyads			(3)
IR (characteristic absorption frequencies)	cm^{-1}	Methylene stretching vibrations, assigned to asymmetric and symmetric CH_2 stretching vibrations	2,958 and 2,933	(4)
		Ester methyl stretching vibrations	2,995, 2,948, and 3,025	
		Carbonyl vibration	1,733	
NMR	ppm	Atactic, vs. TMS	1.9	(5)
		Syndiotactic	–	
		Isotactic, pair of doublets, vs. TMS	1.5–2.5	
Effects of radiation	$C\ cm^{-2}$	Sensitivity to electron beam at an electron-beam energy of 25 keV	10^{-5}	(6)
		Main chain scission (0.5 J cm^{-2} at 26 keV)	0.46	(6)
	Å	UV		(7)
		50%	2,000	
		57%	2,200	
		78%	2,400	
		78%	2,600	
		78%	3,000	
		Main chain scission (4–6 eV, 0.6 J cm^{-2})	0.22	(6)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Effects of radiation	—	Ion beam (0.48 J cm^{-2}; 300 keV)	0.75	(6)
	%	Effective visible range		—
		Transmission	92	
		Haze	2	
Density	g cm^{-3}	—	1.17–1.20	(8)
Glass transition temperature	K	Atactic polymer	379	(8)
			387.3	(9)
			386	(10)
		Isotactic polymer	318	(1, 10)
			324	(11)
		Syndiotactic polymer	120 –>140°C	(1, 10, 11)
Heat deflection temperature	K	1.82 MPa	341.3–371.9	(8)
Dielectric constants	—	50 Hz, 25°C	3.5–3.7	(12–14)
		1,000 Hz	3.3	(14)
		1.0×10^6 Hz	2.2–2.5	(14)
Water absorption	%	1/8 in bar, 24 h	0.3–0.4	(8)
			2	(13)
			0.1–0.3	(14)
Thermal expansion coefficient	—	—	$6 \times 10^{-4} > T_g$	(12)
			$2\text{–}3 \times 10^{-4} < T_g$	
Crystalline structures for PMMA	—	—	Isotactic PMMA	—
		Only in crystalline phase when complexed with various solvents	Syndiotactic PMMA	(15, 16)
Unit cell parameters	Å	Isotactic isomer	$a = 20.98$, $b = 12.06$, c (fiber axis) $= 10.40$	(17)
		With chloroacetone	$a = 25.8$, $b = 35.1$,	(16)
		Irrespective of the type of solvent	$c = 35.4$ (fiber repeat)	(16)
Index of refraction	—	—	1.49	(8, 12)
Tensile strength	MPa	—	48–76	(1, 8)
Fracture toughness	MPa $m^{1/2}$	23°C, air	1.21	(9)
		37°C, water	1.76	
Elongation	%	—	2–10	(8)
Tensile modulus	MPa	—	3,100	(8)
		23°C, air	3,180	(9, 14)
		37°C, water	2,700	(9, 14)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Poisson's ratio	—	—	0.35	(14)
Flexural modulus	MPa	—	2,900–3,100	(1)
Melt flow rate	—	Low heat-resistance material High heat-resistance material	20–30 2–4	(1)
Notched impact strength	$J\,m^{-1}$	—	16–27	(8)
Continuous use temperature	K	—	364–382	(1)
Typical solvents	Ethanol, isopropanol, methyl ethyl ketone, formic acid, nitroethane Any alcohol solution containing 10% alcohol may attack PMMA			(14)
Typical nonsolvent	Turpentine, carbon tetrachloride, butylene glycol, diethyl ether, isopropanol ether, *m*-cresol			—
Suppliers	DuPont, Rohm and Haas, Continental			

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Poly(4-methyl pentene-1)

D. R. PANSE AND PAUL J. PHILLIPS

ACRONYMS, ALTERNATIVE NAME, TRADE NAME PMP, P4MPE, polymethylpentene, TPX, Crystalor

CLASS Poly(α-olefins)

STRUCTURE OF REPEAT UNIT $[-CH_2-CH-]$ with pendant $CH_2CH(CH_3)_2$ on CH

MAJOR APPLICATIONS Hypodermic syringes, needle hubs, blood collection and transfusion equipment, pacemaker parts, cells for spectroscopic and optical analysis, laboratory ware, light covers, automotive components.

PROPERTIES OF SPECIAL INTEREST High optical transparency, excellent dielectric properties, high thermal stability, chemical resistance, crystalline density lower than amorphous density.

PREPARATIVE TECHNIQUES (a) Coordination polymerization: catalytic systems used = α- and δ-$TiCl_3$ in combination with $Al(C_2H_5)_3$ and $Al(C_2H_5)_2Cl$, VCl_3-Al(*i*-$C_4H_9)_3$, modified supported catalysts such as $TiCl_4/MgCl_2$-$Al(C_2H_5)_3$ modified by aromatic acid esters, diesters. Temperature = 30–70°C.[1,2]

(b) Cationic polymerization: catalysts = $AlCl_3$, $AlBr_3$, $AlC_2H_5Cl_2$ and cocatalysts RCl with R = CH_3, C_2H_5, C_6H_5, etc.[1]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Typical comonomers used	—	—	1-Hexene, 1-pentene, 1-octene, 1-decene, 1-octadecene	—
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	84.16	—
Stereoregularity	% isotactic	Catalyst system		
		d-$TiCl_3$-Al(*i*-$C_4H_9)_3$	60	(3)
		δ-$TiCl_3$-$Al(C_2H_5)_2Cl$	90	(4)
Typical molecular weight range	$g\,mol^{-1}$	Cationic polymerization	2,000–250,000	(1)
Polydispersity index	—	Cationic polymerization at:		(1)
		−78°C	2.76	
		−50°C	2.85	
		+5°C	4.11	
Thermal expansion coefficient	K^{-1}	ASTM D696	1.17×10^{-4}	(1, 5)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Reducing temperature	K	Temperature range = 235–320°C	11,481	(6)
Reducing pressure	Pa	Pressure range = 0–200 MPa	453×10^6	(6)
Reducing volume	$cm^3\ g^{-1}$	None given	1.2303	(6)
Amorphous density	$g\ cm^{-3}$	None given	0.838	(7)
Solvents	—	Above 100°C	Cyclohexane, tetralin, decalin, xylenes, chlorobenzene	(7)
Nonsolvents	—	At 20°C	Any organic solvent	(7)
Solubility parameter	$(MPa)^{1/2}$	None given	15.14–16.36	(8)
Theta temperature Θ	K	90–94% isotactic polymer		(9)
		Solvent/method		
		Diphenyl/PE, VM	467.6	
		Diphenyl ether/PE, VM	483	
		Diphenyl methane/PE, VM	449.6	

Mark-Houwink parameters: K and a[9]

Solvent/method	Temperature (°C)	Mol. wt. $\times 10^{-4}$	$K \times 10^3$ (ml g^{-1})	a
Biphenyl/OS	194.6 = Θ*	30	152	0.5
Decalin/OS	130	30	19.5	0.75
Diphenyl ether/OS	210 = Θ*	30	158	0.5
Diphenyl methane/OS	176.6 = Θ*	30	160	0.5

*Theta temperature.

Crystalline state properties[10]

Crystal property	Units	Isotactic	Syndiotactic
Lattice	—	Tetragonal	Not given
Unit cell dimensions	Å	a = 18.6–18.7 b = 18.6–18.7 c = 13.8	—
Unit cell angles	Degree	$\alpha = \beta = \gamma = 90$	Not given
Monomers per unit cell	—	28	Not given
Space group	—	S4-1	Not given
Helix conformation	—	7_2	24_7
Crystalline density at 23°C	$g\ cm^{-3}$	0.814	Not given

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Degree of crystallinity	%	Annealed	70	(11)
		Strongly oriented fiber	85	
		Moldings	55–60	
Heat of fusion	$kJ\,mol^{-1}$	–	5.297	(12)
		Clapeyron equation	5.205	(11)
Entropy of fusion	$kJ\,K^{-1}\,mol^{-1}$	–	10.1×10^{-3}	(12)
		Clapeyron equation	10.3×10^{-3}	(11)
Glass transition temperature	K	DSC	323	(13)
			303	(14)
Melting point	K	Isotactic polymer	518	(1)
Sub-T_g transition temperatures	K	Not given	153–123	(1, 7)
			23	
Crystalline phase disordering temperature	K	Not given	403–453	(7)
Heat capacity	$kJ\,K^{-1}\,mol^{-1}$	Temperature (K)		(14)
		80	0.0472	
		180	0.0917	
		250	0.121	
		300	0.145	
Deflection temperature	K	Under flexural load:		(1)
		0.46 MPa	353–363	
		1.82 MPa	321–323	
Tensile modulus	MPa	ASTM D638	1,500–2,000	(1)
Bulk modulus	MPa	Not given	2,670	(1)
Tensile strength	MPa	ASTM D638		(1)
		At yield	23–28	
		At break	17–20	
Elongation at break	%	Not given	10–25	(1)
Flexural strength	MPa	ASTM D790	25–35	(1)
Flexural modulus	MPa	ASTM D790	1,300–1,800	(1)
Notched Izod impact strength	$kJ\,m^{-1}$	ASTM D256	100–200	(1)
Rockwell hardness	–	None given	L80–90	(5)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Poisson ratio	—	At RT and ambient pressure	0.34	(15)
			0.43	(16)
Shear modulus	MPa	At RT and ambient pressure	970	(1)
Index of refraction *n*	—	Isotactic polymer	1.463	(7)
Haze	%	ASTM D1003	1.2–1.5	(7)
Optical transparency	%	ASTM D1003	90–92	(7)
Dielectric constant	—	25°C, 102–106 Hz	2.12	(1)
Dielectric loss factor	—	At 20°C		(5)
		Frequency range		
		50 Hz	60×10^{-6}	
		1 kHz	$(35–140) \times 10^{-6}$	
		1 MHz	$(25–50) \times 10^{-6}$	
Dielectric breakdown voltage	kV mm^{-1}	None given	42–65	(5)
Volume resistivity	Ohms cm	None given	>1,016	(5)
Surface tension	mN m^{-1}	At 20°C, contact angle method	25	(5)
Thermal conductivity	W m^{-1} K^{-1}	ASTM C177	0.167	(5)
Permeability coefficient	m^3 (STP) m s^{-1} m^{-1} Pa^{-1} ($\times 10^{-16}$)	Film thickness = 78 μm		(17)
		Permeant		
		O_2	317.2	
		N_2	74	
		He	1020	
		H_2	1342	
		CO_2	960	
Gas separation factor	—	Gas 1/Gas 2		(18)
		O_2/N_2	4.1	
		H_2/N_2	16.5	
		CO_2/N_2	8.6	
		CO_2/O_2	2.1	
		H_2/O_2	4.1	
		H_2/CO_2	1.9	
Melt index	g (10 min)$^{-1}$	At 260°C, 5 kg load	20	(5)
Speed of sound	m s^{-1}	Longitudinal	2,180	(15)
		Shear	1,080	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Pyrolyzability, amount of product	%	Name of product		(19)
		Propene	0.8	
		Propane	33.9	
		2-Methylpropene	55.6	
		2-Methylpropane	3.5	
		2-Methylbutene	2.0	
		Pentane	0.3	
		4-Methyl 1-pentene	2.2	
		2,3-Dimethylbutane	1.0	
		Others	0.7	
Vicat softening point	K	ASTM D1525	446	(5)
Degradation temperature	K	—	553	(1)
Radiation G (product)	—	Per 100 eV of absorbed radiation	0.3	(20)
$G(S)/G(X)$	—	Irradiated in air	0.6	(20)
Water absorption	%	Saturation	0.01	(1)
Flammability, flame propagation rate	cm min^{-1}	ASTM D635	2.5	(5)

Suppliers and quantities produced

Supplier	Trade Name	Amount (tons per year)
Mitsui Petrochemical Industries (Japan)	TPX	~22,700
Phillips 66 (USA)	Crystalor	—
British Petroleum Co.	—	~25,000

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Poly(methylphenylsiloxane)

ALEX C. M. KUO

ACRONYM, ALTERNATE NAMES, TRADE NAMES PMPS; poly[oxy(methylphenylsilylene)]; methylphenyl silicone oil; Dow Corning® 710 Fluid

CLASS Polysiloxanes

STRUCTURE $-[(CH_3)(C_6H_5)Si-O-]_n$

CAS REGISTRY NUMBER [9005-12-3]

MAJOR APPLICATIONS Heat exchange fluids; high temperature lubricating oil for instruments, bearings, and timers; glass sizing agents; greases; hydraulic fluids.

PROPERTIES OF SPECIAL INTEREST Thermal stability. Oxidative stability. Wide serviceable temperature (−70 to 260 °C) and minimal temperature effect. Good resistance to UV radiation. Good damping behavior. Excellent antifriction and lubricity, and good dielectric strength.

PREPARATIVE TECHNIQUES Monomer: dichloromethylphenylsilane, methylphenylsiloxane diol, methylphenylcyclotrisiloxane, methlyphenylcyclotetrasiloxane. Polymerization: hydrolysis, polycondensation, ring-opening polymerization.[1]

^{29}Si NMR spectroscopy for typical structural building units in polymethylphenylsiloxanes[2, 3]

Structure	Notation*	Chemical shifts (ppm down-field from TMS)
$-Si(CH_3)_2-(C_6H_5)$	M^{ph}	−1
$-Si(C_6H_5)_2-(CH_3)$	M^{ph_2}	−11
$-Si(C_6H_5)_3$	M^{ph_3}	−21
$-[O-Si(CH_3)(C_6H_5)]-$	D^{ph}	−31 to −35
$[O-Si(CH_3)(C_6H_5)-]_3$	D_3^{ph}; cyclic trimer	−21
$[O-Si(CH_3)(C_6H_5)-]_4$	D_4^{ph}; cyclic tetramer	−30.5
$(-O_{0.5}-)_3Si-C_6H_5$	T^{ph}	−77 to −82
$(-O_{0.5}-)_4Si$	Q	−105 to −115

*See shorthand notation for siloxane polymer unit in the *Polydimethylsiloxane* entry in this handbook.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Infrared absorption	cm^{-1}	Si−O−Si	1,000–1,130	(4, 5)
		$Si-(C_6H_5)$	3,020–3,080; 1,590; 1,430; 1,120; 700; 730	
		$Si-(CH_3)$	760–845; 1,245–1,275	
		Si−H	2,100–2,300; 760–910	
		Si−OH	3,200–3,695; 810–960	
		$Si-CH=CH_2$	1,590–1,610; 990–1,020; 980–940	
Ultraviolet (UV) absorption	nm	$Si-(C_6H_5)$	270; 264; 259	(6)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	PMPS (102 cs) at 20°C	1.0787	(7)
		PMPS (500 cs) at 25°C	1.11	(8)
		PMPS ($M_w = 3.27 \times 10^5$) at 25°C	1.115	(9)
Density-molecular weight-temperature relationship	$g\,cm^{-3}$	Material: trimethylsiloxy-ended PMPS at 0–60°C	$1/\rho = 0.7303 + (4.4893 \times 10^{-4})T + (0.1814T + 16.3684)/M$	(10)
Solvents	Toluene, chloroform, diethyl ether, ethyl acetate, acetone (hot)			(11, 12)
Nonsolvents	Methanol, ethanol, *n*-propanol, perfluoro methylcyclohexane, ethylene glycol			(11, 12)
Solubility parameter δ	$(MPa)^{1/2}$	Silica filled PMPS elastomer measured by swelling	18.4	(12)
Theta temperature Θ	K	Diisobutylamine	303.4	(13)
Second virial coefficients A_2	$mol\,cm^3\,g^{-2}$	PMPS ($M_n = 4.06 \times 10^5$) in cyclohexane at 25°C	1.52×10^{-4}	(13)
Characteristic ratio, $C_\infty = \langle r^2 \rangle / nl^2$	–	Undiluted PMPS with 100 bonds equilibrated at 383 K	10.7	(14)
Root-mean-square end-to-end chain length, $(\langle r^2 \rangle / M)^{1/2}$	$nm\,mol^{1/2}\,g^{-1/2}$	PMPS at 25°C	5.65×10^{-2}	(13)
		Value calculated for $l = 1.65$ Å, $\theta_1 = 110°$, $\theta_2 = 143°$	3.63×10^{-2}	
Z-average radius of gyration $\langle s^2 \rangle_z$	–	PMPS in benzene-d_6 at 293 K ($M_z = 3{,}890$)	11.9	(15)
		PMPS in benzene-d_6 at 293 K ($M_z = 8{,}500$)	18.6	(15)
		PMPS in benzene-d_6 at 293 K ($M_z = 21{,}130$)	26.7	(15)

Mark-Houwink parameters: *K* and *a*

Solvents	Temp. (°C)	$K \times 10^3$ (ml g^{-1})	*a*	Reference
Toluene	25°C	3.90	0.78	(13)
Diisobutylamine	30.4°C	51.5	0.50	(13)
Cyclohexane	25°C	5.52	0.72	(13)
Cyclohexane	25°C	27.3	0.60	(16)
Cyclohexane	50°C	15.6	0.65	(16)
Methylcyclohexane	20°C	30.6	0.58	(16)
THF	25°C	16.5	0.69	(16)
Toluene	25°C	12.3	0.684	(17)
Toluene	25°C	6.7	0.78	(18)
Benzene	20°C	110.6	0.57	(18)

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Interaction parameter χ_{12}	—	Compound pair	Temp. (K)	Method		
		PMPS network/toluene	298	Swelling	0.485	(6)
		PMPS network/benzene	298	Swelling	0.489	(6)
		PMPS network/chloroform	298	Swelling	0.496	(6)
		PMPS network/cyclohexane	298	Swelling	0.632	(6)
		PMPS network/hexane	298	Swelling	0.891	(6)
		$MD_{28}^{ph}M/MD_{13}M$	Critical point, $T_c = 518$	Light scattering	0.112	(19)
		$MD_{23}^{ph}M/MD_{13}M$	Critical point, $T_c = 458$	Light scattering	0.122	(19)
		$MD_{23}^{ph}M/M^{OH}D_{15}M^{OH}$	Critical point, $T_c = 446$	Light scattering	0.111	(20)
		$MD_{23}^{ph}M$/PDMS ($M = 1{,}420$; cyclic)	Critical point, $T_c = 442$	Light scattering	0.095	(21)
		$MD_{3}^{ph}M$/PDMS network	298	Swelling	0.345	(22)
		$MD_{2}^{ph}M$/PDMS network	298	Swelling	0.438	(22)
		$MD^{ph}M$/PDMS network	298	Swelling	0.356	(22)
Enthalpy of fusion ΔH_u	$J\,g^{-1}$	Semicrystalline PMPS			4.5	(17)
Viscosity temperature coefficient (VTC)	—	$MD_{3}^{ph}M$			0.692	(10)
		PMPS (500 cs)			0.79	(8)
		PMPS (482 cs)			0.88	(23)
		Copolymer of 50% phenylmethyl and 50% dimethyl siloxane (115 cs)			0.78	(23)
Activation energies for viscous flow ΔE_{visc}	$kJ\,mol^{-1}$	PMPS polymer			50.2	(24)
		PMPS polymer			49.8	(25)
Coefficients of cubical expansion α	K^{-1}	102 cs PMPS at 20°C			7.1×10^{-4}	(12)
		500 cs PMPS (273–428 K)			7.7×10^{-4}	(7)
		PMPS rubber from −20 to 25°C			4.69×10^{-4}	(26)
		Peroxide cure PMPS rubber from 30–90°C			8.52×10^{-4}	(27)
		Copolymer of 35% methylphenyl and 65% dimethyl siloxane at 20°C			7.6×10^{-4}	(28)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature T_g	K	PMPS ($M \rightarrow \infty$)	251.3	(17)
		PMPS ($M_n = 27{,}300$)	247	(29)
		PMPS ($M_n = 93{,}000$)	240.5	(30)
Melting point T_m	K	Semicrystalline PMPS	308	(17)
Coefficient of isothermal compressibility β	atm^{-1}	Copolymer of 35% methylphenyl and 65% dimethyl siloxane at 20°C	7.1×10^{-5}	(28)

Compressibility[8]

Pressure (psi)	Material	Compressibility (%)	Bulk modulus, secant method (psi)
1,000	PMPS (500 cs)	0.4	250,000
5,000	PMPS (500 cs)	1.7	294,000
10,000	PMPS (500 cs)	3.15	317,000
20,000	PMPS (500 cs)	5.5	364,000

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Water contact angle θ	Degrees	PMPS film on soda-lime glass, after 15 min treatment at:		(31)
		100°C	77	
		200°C	81	
		300°C	83	
		400°C	81	
		450°C	60	
		475°C	0	
Surface tension γ	$mN\,m^{-1}$	102 cs PMPS at 20°C	26.1	(7)
		500 cs PMPS at 25°C	28.5	(8)
Temperature coefficient of surface tension $-d\gamma/dT$	$mN\,m^{-1}\,K^{-1}$	PMPS (50–102 cs) at 20°C	0.11	(7)
Flash point	K	500 cs PMPS	575	(8)
Pour point, open cup	K	500 cs PMPS	251	(8)
Refractive index n_D^{25}	–	$MD_2^{ph}M$ at 25°C	1.4744	(10)
		$MD_3^{ph}M$ at 25°C	1.4889	(10)
		PMPS (500 cs) at 25°C	1.533	(8)
		PMPS ($M = 4 \times 10^4$)	1.550	(32)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	500 cs PMPS at 50°C	0.147	(8)

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PROPERTY	UNITS	CONDITIONS	VALUE			REFERENCE
Specific heat at 100°C	$kJ\,kg^{-1}\,K^{-1}$	500 cs PMPS at 40°C	1.52			(8)
		500 cs PMPS at 100°C	1.901			
		500 cs PMPS at 200°C	2.115			
Radiation resistance	rads	500 cs PMPS	2.0×10^8			(8)
Diamagnetic susceptibility X_m	$cm^3\,g^{-1}$	PMPS fluid	0.597×10^{-6}			(33)
Sound velocity	$m\,s^{-1}$	At 25°C, 500 cs PMPS	1,372			(8)
X-ray diffraction pattern	Å	Semi-crystalline PMPS	8.33, 7.69, 4.83, 4.40, 3.8			(17)
Color	APHA	500 cs PMPS	40			(8)
Gas solubility coefficient *S*	cm^{-3} (STP)/cm^3 polym. atm		10°C	35°C	55°C	(34)
		CO_2	1.19	0.81	0.76	
		CH_4	0.3	0.25	0.20	
		C_3H_8	8.57	3.79	2.65	

Gas permeability coefficient of silica filled PMPS membrane, at 35°C[35, 36]

Gas	$Pr \times 10^8$ (cm^3 (STP) cm/s cm^2 cm Hg)	Gas	$Pr \times 10^8$ (cm^3 (STP) cm/s cm^2 cm Hg)
NH_3	10.97	CH_4	0.36
H_2S	8.73	O_2	0.32
C_3H_8	1.39	N_2	0.103
C_2H_6	0.91	H_2	1.15
CO_2	2.26	He	0.35
C_2H_4	0.93	—	—

WLF parameters for PMPS

M_n	T_0 (K)	C_1	C_2/K	T_g (K)	$a_{T,\alpha}$ method	Reference
5,000	181.2	20.4	56.76	223.3	Photon correlation spectroscopy	(37, 38)
12,000	237.4	23.96	48.8	237.4	Dynamic mechanical measurement	(37, 39)
12,000	258.4	7.32	32.5	237.4	Data from dielectric relaxation	(37, 39)
27,300	273.2	14.8	66.4	247.2	Photon correlation spectroscopy	(29)
27,300	248.2	14.8	55.9	248.2	Photon correlation spectroscopy	(29)
27,300	273.2	11.8	67.9	247.2	Data from dielectric relaxation	(29)
130,000	243.2	17.69	34.71	243.2	Dynamic mechanical measurement	(37, 39)
130,000	261.8	7.47	36.1	243.2	Data from dielectric relaxation	(37, 39)

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Dielectric constant and dissipation factor of PMPS (500 cs) at 25°C[40]

Property	Frequency (Hz)								
	1×10^2	1×10^3	1×10^4	1×10^5	1×10^6	1×10^7	3×10^8	3×10^9	1×10^{10}
Dielectric constant	2.98	2.98	2.98	2.98	2.98	2.97	2.93	2.79	2.60
Dissipation factor ($\tan\delta \times 10^4$)	13	1.6	0.7	3	10	50	200	140	170

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Lubricity	mm	Shell four-ball test (wear scar)		(1)
		Steel on steel, PMPS-co-PDMS (25 mol% phenyl) at 1 h/600 rpm/ 50 kg load/ambient temperature	4.18	
		Steel on bronze, PMPS-co-PDMS (25 mol% phenyl) at 1 h/600 rpm/ 10 kg load/ambient temperature	2.53	
		Steel on steel, PMPS-co-PDMS (40 mol% phenyl) at 1 h/600 rpm/ 50 kg load/ambient temperature	4.13	
		Steel on bronze, PMPS-co-PDMS (40 mol% phenyl) at 1 h/600 rpm/ 10 kg load/ambient temperature	0.42	
Dielectric strength	$kV\,cm^{-1}$	500 cs PMPS	137.8	(8)
Volume resistivity	$ohm\,cm^{-1}$	500 cs PMPS	1.0×10^{13}	(8)
Optical configuration parameter Δa	cm^3	PMPS ($M = 4 \times 10^4$) in benzene solution	-17×10^{-25}	(32)
		PMPS ($M = 6 \times 10^4$) with 50 % substitution of dimethlysiloxane in benzene	-5.1×10^{-25}	(32)
		Peroxide cure PMPS network at 25°C	-1.21×10^{-25}	(9)
		Peroxide cure PMPS network at 50°C	-1.27×10^{-25}	(9)
		Peroxide cure PMPS swelled in decalin at 25°C	-0.85×10^{-25}	(9)
		Theoretical value for PMPS	-1.16×10^{-25}	(9)
Stress-optical coefficient C	$m^2\,N^{-1}$	PMPS network at 25°C	5.73×10^{-9}	(9)
Root-mean square dipole moment ratio $\langle \mu^2 \rangle_0 / nm^2$	–	PMPS ($M_w = 1.2 \times 10^5$) in cyclohexane at 25°C	0.31	(41)
Decomposition products	Mixture of stereoisomeric cyclic trimers and tetramers with small amount of pentamer, benzene, and two more complex oligomers (conditions: random scission at $T > 300$°C)			(42)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Thermal decomposition point	K	500 cs PMPS	644	(8)
Spontaneous ignition temperature	K	500 cs PMPS	760	(8)
Activation energy of depolymerization	$kJ\,mol^{-1}$	Trimethylsiloxy end-blocked PMPS	180	(43)
Fire parameters (cone calorimeter test)		External heat flux $60\,kW\,m^{-2}$		(44)
Peak rate of heat release	$kW\,m^{-2}$		90	
Yield of carbon monoxide	$kg\,kg^{-1}$		0.016	
Specific extinction area	$m^2\,kg^{-1}$		1800	

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Poly(methylphenylsilylene)

ROBERT WEST

ACRONYM, ALTERNATIVE NAME PMPS, polymethylphenylsilane

CLASS Polysilanes

STRUCTURE $[-CH_3SiC_6H_5-]$

MAJOR APPLICATIONS Hole transport agent in electrophotography, light-emitting diodes, display devices, and printing processes.

PROPERTIES OF SPECIAL INTEREST Good film-forming characteristics and efficient hole conductor.

GENERAL INFORMATION Polysilanes, or poly(silylene)s, are polymers in which the entire main chain is made up of silicon atoms. This structure permits delocalization of the σ-electrons, giving the polysilanes unique electronic properties. Polysilanes have strong UV absorption bands in the near UV region (~300–400 nm). The excitation energy depends on the polymer chain conformation, which may change with temperature, so many polysilanes are thermochromic. Polysilanes undergo photodegradation with UV light; they can be patterned in photolithographic processes and used as free-radical photoinitiators. They are excellent hole conductors, and display nonlinear optical behavior.

For an overview of polysilanes, see references (1, 2, 3).

Preparative techniques

REACTANTS	TEMP. (°C)	YIELD (%)	$M_w \times 10^{-3}$	REFERENCE
$PhMeSiCl_2$, Na, toluene	110	41	200, 6	(4)
$PhMeSiCl_2$, Na, Et_2O, 15-crown-5	35	88	66	(5)
$PhMeSiCl_2$, Na, toluene (15% heptane), 15-crown-5	65	40	10.2	(6)
$PhMeSiCl_2$, Na, toluene, ultrasound	110	55	107, 3.3	(7)
$PhMeSiCl_2$, Na, toluene, 2% EtOAc	110	16	431, 11.6	(8)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Repeat unit	$g\,mol^{-1}$	$C_6H_5SiCH_3$	120	–
Molecular weight	Varies greatly depending on polymerization conditions			
Polydispersity	Varies greatly depending on polymerization conditions			
Glass transition temperature T_g	K	Polymer is ordinarily atactic and amorphous	~393	–

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melting temperature, T_m	K	Polymer is ordinarily atactic and amorphous	~493	–
Infrared spectrum	cm^{-1}	–	3,030, 2,960, 2,870, 2,000–1,660, 1,600, 1,530, 1,430, 1,100, 1,265, 830–650, 430	(7)
UV absorption	nm	$M_w = 10^6$	342	(9)
		$M_w = 10^4$; 9,300 (ε = repeat)	341	(5, 9)
		$M_w = 10^3$	332	(9)
Emission spectrum	nm	2-MeTHF solution, $\phi = 0.75$, $\tau = 0.025$ ps	353	(1)
		Solid, 77 K	350, 480	(10)
		Solid, 298 K	365, 530	(11)
NMR spectra	δ (ppm)	Nucleus / Condition		
		^{29}Si / C_6D_6	−39.2, −39.9, −41.2	(4, 7)
		^{13}C / C_6D_6	−6.7 to −5.4	(7)
		^{13}C / C_6D_6	127.6–129.3	(7)
		^{13}C / C_6D_6	135.0–136.3	(7)
		^{1}H / C_6D_6	0.5–1.0, b, CH_3	(7)
		^{1}H / C_6D_6	6.0–7.5, b, C_6H_5	(7)
Solvents	THF, toluene, CH_2Cl_2, hexane, 25°C			
Nonsolvents	Ethanol, 2-propanol			
Properties from light scattering study				(12)
M_w	$g\,mol^{-1}$	THF solution	46,000	
M_w/M_n	–	–	4.2	
$10^4\ A_2$	$mol\,cm^3\,g^{-2}$	–	3.6 ± 0.5	
R_g	nm	–	21	
R_g°, w	nm	–	15	
C_∞	–	–	64 ± 20	
Electrical conductivity	$S\,cm^{-1}$	Doped with SbF_5	2×10^{-4}	(13)
Hole drift mobility	$cm^2\,V^{-1}\,s^{-1}$	$M_w = 69,000$, field = $2 \times 10^5\,V\,cm^{-1}$, 298 K	2×10^{-4}	(14)
		$M_w = 11,000$	7×10^{-5}	
Surface tension	$mN\,m^{-1}$	–	43.3, 44.1	(15)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Scission, quantum yield, ϕ_s	mol Einstein^{-1}	THF solution, $\lambda = 313$ nm Solid, $\lambda = 313$ nm	0.97 0.015	(1)
Cross-linking, quantum yield, ϕ_x	mol Einstein^{-1}	THF solution, $\lambda = 313$ nm Solid, $\lambda = 313$ nm	0.12 0.002	(1)
Suppliers	Nippon Soda Co. Ltd., 2-1, Ohtemachi 2-chome, Chiyoda-ku, Tokyo 100, Japan Gelest Inc., 612 William Leigh Drive, Tullytown, PA 19007-6308, USA			

Nonlinear optical properties[16]

M_w (g mol^{-1})	Temp. (°C)	λ (nm)	Lp (nm)	X^{131} (esu)
>300,000	23	1,064	120	7.2×10^{-12}
–	23	1,907	120	4.2×10^{-12}
–	23	1,907	1,200	1.9×10^{-12}

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Poly(methylsilmethylene)

Q. H. SHEN AND L. V. INTERRANTE

ACRONYMS PC, PCS

CLASS Polycarbosilanes

STRUCTURE $Si(Me)HCH_2$ (branched, partially *x*-linked)

PREPARATIVE TECHNIQUES The polycarbosilane* employed to make commercial Nicalon SiC ceramic fiber is prepared via thermally induced rearrangement reaction of poly(dimethylsilane) or dodecamethylcyclohexasilane.

MAJOR APPLICATION Precursor for the commercial Nicalon™ fiber, SiC composites. The polymer itself is no longer available for sale in the United States and Canada.

PROPERTIES OF SPECIAL INTEREST Relatively low cost. High yield for SiC ceramic. Fuseable solid, soluble in hydrocarbons. Poor resistance to base and oxidation by air.

PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Molecular weight, M_n	$g\ mol^{-1}$	Polymer	Starting materials	Reaction temp. (°C)		
		PC-450	Polydimethylsilane	450	1,250	(1)
		PC-460	Polydimethylsilane	460	1,450	(1)
		PC-470	Polydimethylsilane	470	1,750	(1)
		PC-B5.5	Polydimethylsilane	320	1,312	(2)
			Borodiphenylsiloxane	—	—	—
		PC-B3.2	Polydimethylsilane	280	1,730	(2)
			Borodiphenylsiloxane	—	—	—
IR (characteristic absorption frequencies)	cm^{-1}	For $SiCH_2Si$			1,050, 1,350,	(1)
		For Si–H			2,100	
NMR spectra	ppm	^{1}H NMR, solution			4.4, 0.2, −0.3	(1)
		^{13}C NMR, solution			3	(3)
		^{29}Si NMR, solution			−0.75 to 0.5; −17.5 to −16.01	(2)
		^{29}Si NMR, solid state			—	(3, 4, 5)
Density	$g\ ml^{-1}$	25°C			1.116	(6)

*Polycarbosilanes with the $[SiMeHCH_2]_n$ formula can also be prepared via the Grignard coupling reaction of $Cl_2(Me)SiCH_2Cl$, followed by reduction with $LiAlH_4$, or via ROP of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane, followed by $LiAlH_4$ reduction, or via chlorination of poly(dimethylsilylenemethylene), followed by reduction with $LiAlH_4$. The products of these latter reactions differ considerably in structure and properties from the ''PCS'' obtained from $[Me_2Si]_n$, have lower yields as SiC precursors, and are not widely used for this purpose.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Decomposition temperatures	K	For cured PC fibers in N_2		(7)
		Starting decomp. temp.	~673	
		Ending decomp. temp.	~1,573	

Pyrolyzability

CONDITIONS	PYROLYSIS TEMP. (K)	VALUE	REFERENCE
Nature of the product (under N_2); PC precursors		Empirical formula for pyrolyzed SiC fibers (amorphous)	(2)
PC-TMS	1,573	$SiC_{1.79}H_{0.037}O_{0.191}$	
PC-470	1,573	$SiC_{1.40}H_{0.046}O_{0.038}$	
PC-B3.2	1,573	$SiC_{1.48}H_{0.139}O_{0.145}$	
PC-B5.5	1,573	$SiC_{1.57}H_{0.051}O_{0.145}B_{0.006}$	
Amount of product (under N_2); PC precursors		Ceramic yield (%)	(2)
PC-470	1,573	54	
PC-TMS	1,573	76	
PC-B-5.5	1,573	61	
PC-B3.2	1,573	64	
Impurities remaining (under N_2)	1,573	Solid impurities Free C, SiO_2	(8, 9)
Gaseous products (under vacuum or N_2)*	673–873	H_2, C_nH_{2n+2}	(2)
	873–1,273	H_2, CH_4	
	1,273–1,573	H_2	
	>1,773	CO	
Gaseous products (under He) from PCS precursors	873	CH_4	(10)
	973	CH_4, C_2H_6, Me_2SiH_2, Me_3SiH, Me_4Si	
	1,073	CH_4, C_2H_6, Me_3SiH, Me_4Si	
	1,273	CH_4, C_2H_6, CO, C_2H_4 Me_3SiH, Me_4Si	

*From PC-470 and PC-B precursors.

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Poly(methylsilsesquioxane)

RONALD H. BANEY

ACRONYM, ALTERNATIVE NAME, TRADE NAME Methyl-T, PMSQ, Glass Resin® (Owens Illinois/Showa Denko)

CLASS Polysiloxanes (siloxane ladder polymers)

STRUCTURE The structure has not been reported in the literature but probably depends upon the method of preparation. Structural studies on methylsilsesquioxane are virtually nonexistent though the term ladder structure is frequently used.[(1)]

MAJOR APPLICATIONS Interlayer dielectrics, high-temperature resins, and organic antireflective coatings.

PROPERTIES OF INTEREST Very high thermal stability (>500°C) and good dielectric properties.

RELATED POLYMERS Poly(alkylsilsesquioxane) and poly-*co*-silsesquioxanes: There are many references to these classes of materials,[(1)] but they are generally poorly characterized. Thus, they are not included in this handbook.

Preparation

Acronym*	Process	Molecular weight ($g\,mol^{-1}$)	Reference
PMSQ-1	H_2O to $MeSiCl_3$ in THF and/or MIBK + Et_3N at 0°C then heat to 110°C	$M_w = 10^5$	(2, 3)
PMSQ-2	Same as PMSQ-1 at 3,000 Pa N_2	$M_w = 10^6$	(4)
PMSQ-3	Two layer system of sodium acetate in H_2O and toluene with 2-propanol	$M_w = 5 \times 10^3$	(58)
PMSQ-4	$MeSiCl_3$ + ethylenediamine (2:1) then hydrolysis in acetone-water-HCl, dried solid heated in xylene at 35°C	$M_w = 10^5$–10^6	(6)
PMSQ-5	$MeSi(OMe)_3$ at interface of aqueous ammonia	Insoluble spheres	(7, 8)
PMSQ-6	Partial hydrolysis and condensation of $MeSi(OMe)_3$	—	(9)
PMSQ-7	$MeSiOAc(OMe)_2$ reacted with $NaHCO_3$ suspended in MIBK at 100°C gave prepolymer which was then heated with 1 wt% KOH	$M_n = 1.4 \times 10^5$	(9)
PMSQ- Insoluble	Direct hydrolysis of $MeSiCl_3$ with no solvent	Insoluble gel	(6)

*See reference (1).

Characteristic IR bands (Si-O-Si stretch) for ''ladder'' structure*

PMSQ-	Characteristic IR (cm^{-1})	*d* spacing (Å)	^{29}Si NMR (ppm)	Reference
1	1,180, 1,020	–	–	(2)
2	1,130, 1,035	–	–	(4)
3	1,125, 1,040	–	–	(5)
4	1,120, 1,030	8.7, 3.6	−55.3, −64.8	(6)
7	1,125, 1,040	–	–	(10)

*Not definitive.

Thermal stability

Material	Conditions	Temp. (°C)		Reference
		Air	N_2	
$MeSiCl_3$ hydrolyzed with ''organic solvent'' and condensed with Et_3N catalyst	Onset, decomposition	460	–	(11)
PMSQ-3	Onset, decomposition	400	660	(5)
PMSQ-4	5% N_2, 9% air	400	400	(6)

Applications

Application	Reference
Resists	(12)
Electrical insulation	(2–5)
Additives for cosmetics	(13)
Additives for toughening plastics	(14, 15)
Cladding for glass fiber	(16)
Ceramic binder	(17)
Si–C–O ceramic precursor	(18)

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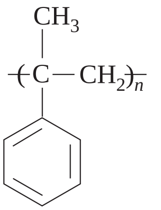
Poly(α-methylstyrene)

LISALEIGH KANE AND RICHARD J. SPONTAK

ACRONYMS PαMS, PAMS

CLASS Vinyl polymers

STRUCTURE



MAJOR APPLICATION Copolymer with styrene for improved heat resistance.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	g cm^{-3}	–	1.07	(1)
Glass transition temperature T_g	K	$\overline{M}_w$ =		
		700,000	435	(2)
		400,000	444	(2)
		113,000	441	(2)
		76,500	447.3	(3)
		61,000	443	(4)
		55,000	442, 453	(5, 6)
		50,000	453	(1)
		25,000	439.5	(3)
		19,500	442	(6)
		6,700	433	(6)
		3,500	414	(6)
		2,510	366.3	(3)
Heat capacity C_p	J K^{-1} mol^{-1}	300 K to T_g	$29.42 + 0.4498T - (1.280 \times 10^6)T^{-2}$	(7)
		T_g to 490 K	$-6.43 + 0.5758T$	
Ceiling temperature	K	–	334	(8, 9)
Depolymerization temperature	K	–	563	(10)
Activation energy for pyrolysis	kJ (per repeat unit)	–	188–243	(11)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Half-life temperature	K	Polymer loses 50% by weight in 40–50 min	560	(10)
Volatilization (per minute)	%	350°C	230	(10)
Dielectric constant	—	—	2.58	(12)
NMR spectroscopy		Solvent = *d*-chloroform, $T = 30°C$, conc. = 10% (w/v)		(13)
		Solvent = chlorobenzene, $T = 120°C$, conc. = 20% (w/v)		(14)
		Solvent = *o*-dichlorobenzene, $T = 100°C$, conc. = 10 wt%		(15)
		Solvent = chlorobenzene-d5, $T = 30, 70°C$, conc. = 7.5% (w/v)		(16)
		Solvent = methylene chloride, $T = -78°C$		(17)
		Solvent = *d*-chloroform, $T = 25°C$		(18)
Flory-Huggins interaction parameter χ	—	Homopolystyrene	0.0323	(19)
			0.047	(1)
		Tetrahydrofuran, $T = 30°C$	0.462	(20)
		α-Chloronaphthalene		(20)
		$T = 30°C$	0.440	
		$T = 45.5°C$	0.428	
		Toluene		(20)
		$T = 30°C$	0.463–0.465	
		$T = 25°C$	0.466	
		Trans-decalin		(20)
		$T = 10°C$	0.500	
		$T = 30°C$	0.473	
		1-Chlorobutane		(20)
		$T = 5°C$	0.492	
		$T = 25°C$	0.490	
		$T = 50°C$	0.489	
		Cyclohexane		(20)
		$T = 46°C$	0.496	
		$T = 39°C$	0.499	
		$T = 38.6°C$	0.500	
		$T = 36°C$	0.500	
		$T = 35°C$	0.500	
		$T = 32°C$	0.503	
		$T = 28°C$	0.506	
		$T = 24°C$	0.508	
		$T = 20°C$	0.509	
		p-Xylene, $T = 30°C$	0.459	(20)
		Nitrobenzene, $T = 30°C$	0.481	(20)
		Chlorobenzene, $T = 30°C$	0.455	(20)
		Tetralin, $T = 50°C$	0.427	(20)
		p-Dioxane, $T = 30°C$	0.463	(20)
		2-Hexanone, $T = 30°C$	0.532	(20)
		n-Butyl acetate, $T = 30°C$	0.526	(20)
		Dimethlyformamide, $T = 30°C$	0.525	(20)

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Poly(α-methylstyrene)

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Solubility parameter	$(MPa)^{1/2}$	–	18.6		(21)
Interaction energy $(P^*)^{1/2}$	$(MPa)^{1/2}$	–	20.7		(21)
Interaction pair $(\delta_i–\delta_j)^2$	MPa	Polyacrylonitrile	93.72		(22)
		Poly(methyl methacrylate)	0.00		
		Tetramethylbisphenol A polycarbonate	0.88		
		Poly(vinyl chloride)	0.293		
		Poly(2,6-dimethyl-1,4-phenylene oxide)	2.18		
		Poly(ε-caprolactone)	0.142		
Second virial coefficient A_2	$mol\,cm^3\,g^{-2}$	n-Butyl chloride, $\overline{M}_w = 6{,}900–3{,}540{,}000\,g\,mol^{-1}$, $T = 25°C$	$(3.11 \times 10^{-3})\overline{M}_w^{-0.255}$		(23)
		Cyclohexane, $\overline{M}_w = 5{,}900–341{,}000\,g\,mol^{-1}$			(24)
		$T = 30°C$	$(5.5 \times 10^{-10})\overline{M}_w^{0.84}$		
		$T = 24°C$	$(6.0 \times 10^{-9})\overline{M}_w^{0.72}$		
		$T = 20°C$	$(2.4 \times 10^{-7})\overline{M}_w^{0.50}$		
		Toluene, $\overline{M}_w = 3{,}000–804{,}000\,g\,mol^{-1}$, $T = 25°C$	$(2.45 \times 10^{-2})\overline{M}_w^{-0.32}$		(25)
Radius of gyration R_g	nm	n-Butyl chloride, $\overline{M}_w = 6{,}900–3{,}540{,}000\,g\,mol^{-1}$, $T = 25°C$	$(2.10 \times 10^{-2})\overline{M}_w^{0.526}$		(23)
		Cyclohexane, $\overline{M}_w = 5{,}900–341{,}000\,g\,mol^{-1}$			(24)
		$T = 36.2°C$	$(2.82 \times 10^{-2})\overline{M}_w^{0.499}$		
		$T = 28°C$	$(4.08 \times 10^{-2})\overline{M}_w^{0.463}$		
		$T = 24°C$	$(4.65 \times 10^{-2})\overline{M}_w^{0.450}$		
		$T = 20°C$	$(6.54 \times 10^{-2})\overline{M}_w^{0.414}$		
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None	n-Butyl chloride, $\overline{M}_w = 6{,}900–3{,}540{,}000\,g\,mol^{-1}$	K	a	(23)
		$T = 25°C$	2.70×10^{-2}	0.590	
		$T = 50°C$	2.65×10^{-2}	0.594	
		$T = 5°C$	3.36×10^{-2}	0.570	
		Toluene, $\overline{M}_w = 26{,}000–603{,}000\,g\,mol^{-1}$, $T = 25°C$	7.81×10^{-5}	0.73	(26)
		Toluene, $\overline{M}_w = 3{,}000–804{,}000\,g\,mol^{-1}$, $T = 25°C$	1.1×10^{-4}	0.71	(25)
Sedimentation constant S	–	Toluene, $\overline{M}_w = 26{,}000–603{,}000\,g\,mol^{-1}$, $T = 25°C$	$(1.72 \times 10^{-2})\overline{M}_w^{0.49}$		(26)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Solvent	–	–	α-Chlorophthalene	(20)
			α-Methyl naphthalene	(10)
			Benzene	(20)
			1-Chlorobutane	(20)
			Chlorobenzene	(14, 20)
			Chloroform	(27, 28)
			Cyclohexane	(20, 26)
			Decalin	(20, 29)
			1,2-Dichloroethane	(30)
			Dichloromethane	(30)
			Dimethylformamide	(20)
			9,10-Dihydroanthracene	(29)
			Diphenylamine	(29)
			Diphenyl ether	(10)
			2-Hexanone	(20)
			Chloride	
			1-Methylnaphthalene	(29)
			2-Naphthol	(29)
			n-Butyl acetate	(20)
			n-Butyl chloride	(23)
			n-Hexane	(27)
			Phenol	(29)
			p-Xylene	(20)
			p-Dioxane	(20)
			Sulfur dioxide (l)	(30)
			Tetralin	(20, 29)
			Tetrahydrofuran	(20, 26, 32, 33)
			Toluene	(10, 20, 34)
			Triphenylmethane	(29)
			1,4-Trichlorobenzene	(10)
Nonsolvent	–	–	Methanol	(28, 32, 35)
Theta temperature Θ	K	Cyclohexane	309.2	(24, 36)
Heat of polymerization ΔH°	$J\,mol^{-1}$	Anionic polymerization, sodium naphthalene complex initiator, THF solution	−25.9	(8)
Entropy of polymerization ΔS°	$J\,mol^{-1}\,K^{-1}$	Anionic polymerization, sodium naphthalene complex initiator, THF solution	−103.8	(8)
Rate of depolymerization $d[M]/dt = 2k_iN[P]$	$mol\,l^{-1}\,h^{-1}$	$T = 236.5°C$		(10)
		α-Methyl naphthalene	$k_i = 0.19 \times 10^{-4}$	
		Diphenyl ether	$k_i = 0.24 \times 10^{-4}$	
		Trichlorobenzene	$k_i = 0.66 \times 10^{-4}$	

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
UCST and LCST	K	For $\overline{M}_w = 114,000\,g\,mol^{-1}$; Solvent =	T_{UCST}	T_{LCST}	(37)
		Cyclopentane	298.7	417.6	
		Cyclohexane	286.5	481.3	
		Trans-decalin	266.6	—	
		n-Butyl acetate	—	452.9	
		n-Pentyl acetate	312.2	475.8	
		n-Hexyl acetate	303.2	500.9	

Thermal degradation (at 275°C)

Solvent	Boiling point (°C)	% Conversion	Reference
2-Naphthol	286	33.1	(29)
Phenol	182	41.9	(29)
1-Methylnaphthalene	242	35.7	(29)
Decalin	187	23.9	(38)
Diphenylamine	302	30.2	(29)
Tetralin	207	33.8	(29)
Triphenylmethane	360	—	(29)
9,10-Dihydroanthracene	312	30.3	(29)

Heats of solution for PαMS/PS solutions and blends at 60°C[34]

PαMS/PS (w/w)	ΔH_{soln} ($J\,g^{-1}$)	ΔH_{blend} ($J\,g^{-1}$)
100/0	—	-15.5 ± 0.3
80/20	-16.5 ± 0.6	-7.4 ± 0.3
50/50	-9.2 ± 0.2	-8.0 ± 0.2
20/80	-8.5 ± 0.5	-7.4 ± 0.5
0/100	—	-6.8 ± 0.3

Polymerization

Initiator	Solvent	T (°C)	$\overline{M}_w/\overline{M}_n$	Reference
Sodium naphthalide	Tetrahydrofuran	—	—	(26, 33, 38, 39)
n-C_4H_9Li	Tetrahydrofuran	−78	<1.1	(32)
	Methylcyclohexane	—	—	(33)
Anionic				
Sodium naphthalene	Tetrahydrofuran	—	1.00–1.03	(8, 26)
sec-Butyllithium	Tetrahydrofuran	−78	1.15	(24)
$TiCl_4$	Methylene chloride	−78	3.54	(40)
$BF_3 \cdot OEt_2$	Hexane/chloroform	−78	—	(40)
BF_3	Hexane/chloroform	−78	—	(40)
BF_3	Toluene	−78	—	(40)
BF_3	Hexane	−78	—	(40)

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Initiator	Solvent	T (°C)	$\overline{M}_w/\overline{M}_n$	Reference
Cationic				
p-Methoxybenzyl chloride	Liquid sulfur dioxide	–	1.02–2.33	(30)
Iodine	Liquid sulfur dioxide	−60	–	(41)
$SnCl_4$ and $SnBr_4$	Methylene chloride	−78	1.93	(31)
	Methylene chloride	−78	1.14	(17)
$SnBr_4$ with chloride-vinyl ether adduct	Methylene chloride	−78	–	(42)
$ZnCl_2$ and $SnBr_4$	Methylene chloride	−78	1.57	(17)
$AlCl_3$	Chloroform	−78, −103	–	(28)
	Toluene	−78, −103	–	(28)
	Toluene	−78	–	(14)
	Carbon disulfide	−50	–	(29)
$B(C_6F_5)_3$	Toluene, dichloromethane	−78, 22	–	(43)

Syndiospecific polymerization

Catalyst system (cationic)	Solvent	T (°C)	Reference
$BF_3 \cdot O(C_2H_5)_2$	Toluene	−78 and −30	(14, 27)
	Methylene chloride	–	(27)
	Toluene/methylcyclohexane	−78 and −30	(14)
	Methylcyclohexane	−78 and −30	(14)
	Methylene chloride	−78	(26)
	Methylene chloride/nitroethane	−78	(27)
$AlCl_3$	Toluene	−75, −78	(14)
	Carbon disulfide	−50	(29)
	Toluene/methylcyclohexane	−78	(14)
$AlBr_3$·trichloroacetic acid	Toluene	−78	(27)
	Methylene chloride	−78	(27)
$TiCl_4$	Toluene	−75, −78	(14, 27)
	Toluene/methylcyclohexane	−78	(14)
	Methylcyclohexane	−78	(14)
	Methylene chloride	−78	(27)
$SnCl_4$	Toluene	−75	(14)
	Toluene/methylcyclohexane	−78	(14)
	Methylcyclohexane	−78	(14)
$SnCl_4$·trichloroacetic acid	Toluene	−78	(27)
	Methylene chloride	−78	(27)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Permeability coefficient P	cm^3 (STP) cm $(cm^2\ s\ cm\ Hg)^{-1}$	35°C, 1 atm		(44)
		He	14.5×10^{-10}	
		CH_4	0.14×10^{-11}	
		O_2	0.82×10^{-11}	
		N_2	0.15×10^{-11}	
		CO_2	3.0×10^{-10}	
Selectivity P_1/P_2	–	35°C, 1 atm		(44)
		He/CH_4	100	
		O_2/N_2	5.4	
		CO_2/CH_4	20.8	
Diffusion coefficient D	$cm^2\ s^{-1}$	35°C, 1 atm		(44)
		CH_4	1.6×10^{-9}	
		O_2	2.1×10^{-8}	
		N_2	4.0×10^{-9}	
		CO_2	7.4×10^{-9}	
Selectivity D_1/D_2	–	35°C, 1 atm		(44)
		O_2/N_2	4.6	
		CO_2/CH_4	4.9	
Solubility coefficient	cm^3 (STP) cm $(cm^3\ atm)^{-1}$	35°C, 1 atm		(44)
		CH_4	0.72	
		O_2	0.30	
		N_2	0.26	
		CO_2	3.0	
Selectivity S_1/S_2	–	35°C, 1 atm		(44)
		O_2/N_2	1.2	
		CO_2/CH_4	4.2	
Suppliers	Aldrich, P.O. Box 355, Milwaukee, Wisconsin 53201, USA. Pressure Chemical Co., 3419 Smallman Street, Pittsburgh, Pennsylvania 15201, USA. Polymer Laboratories Inc., Amherst Fields Research Park, 60 Old Farm Road, Amherst, Massachusetts 01002, USA. Polysciences, Inc., 400 Valley Road, Warrington, Pennsylvania 18976, USA. Scientific Polymer Products, Inc., 6265 Dean Parkway, Ontario, New York 14519, USA.			

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Poly(*p*-methylstyrene)

ARCHIE P. SMITH AND RICHARD J. SPONTAK

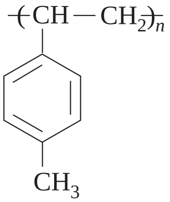
ACRONYMS P*p*MS, PMS, P4MS, MST, *p*MS, P-*p*MS, PPMS, 4MS, P*p*MeS

CLASS Vinyl polymers

CAS NUMBER 24936-41-2

CAS NAME Benzene, 1-ethenyl-4-methyl homopolymer

STRUCTURE



MAJOR APPLICATIONS Similar to polystyrene (PS) (e.g., molded objects, foam drinking cups, and packaging materials). Has a slightly higher deformation temperature and flame resistance than PS.

POLYMERIZATION METHOD	CONDITIONS	REFERENCE
Cationic photopolymerization	Cationic polymerization using phosphonium and arsonium salts as initiators. Illuminated with Xenon Arc lamp at 25°C	(1)
Living carbocationic	Polymerization in methyl chloride/methyl cyclohexane solution at −80°C without initiator and with $TiCl_4$ as initiator	(2)
Radical polymerization	Bulk polymerization using azobisisobutyronitrile as initiator at 50°C	(3)
Cationic polymerization by radiation	Polymerization of both wet and dry monomers by exposure to ^{60}Co γ-ray radiation	(4)
Cationic polymerization	Polymerization conducted in various solvents with acetyl perchlorate or iodine at 0°C	(5)
Cationic polymerization	Emulsion polymerization performed with hydrogen iodide/zinc halide initiators in toluene or methylene chloride at various temperatures	(6)
Radical polymerization	Isothermal solution polymerization in cyclohexane with AIBN initiator	(7)
Radical polymerization	Solution polymerization in benzene using azobisisobutyronitrile as initiator at 50°C	(8)

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Propagation and termination constants

K_p	$K_t \times 10^{-6}$	$K_p/K_t \times 10^6$	T (°C)	Method*	Reference
84	66	1.28	30	A	(9)
103	—	—	40	B	(10)
135	—	—	50	B	(10)
188	—	—	60	B	(10)
266	—	—	70	B	(10)

*A = intermittent photoionization via flashing light; B = Smith-Ewart volume in emulsion polymerization.

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Transfer constants to solvents C_s	—	Solvent ($T = 60$°C)			(11)
		p-Isopropyl anisole	3.27×10^{-4}		
		p-Diisopropyl benzene	7.34×10^{-4}		
		p-Isopropyl benzonitrile	26.0×10^{-4}		
		Cumene	4.12×10^{-4}		
		p-Bromocumene	9.23×10^{-4}		
		p-Chlorocumene	7.67×10^{-4}		
Free radical copolymerization reactivity ratios: r_1 and r_2	—	Comonomer	r_1	r_2	
		Acrylate, methyl	1.540	0.170	(12)
		Methacrylate, methyl	0.440	0.400	(13)
		N,N Divinylaniline	11.8	0.05	(14)
		p-Chlorostyrene	0.610	1.150	(13)
		Vinyl methyl sulfoxide	2.730	0.010	(15)
Typical comonomers	—	—	*p*-Bromostyrene		(16)
			p-Chlorostyrene		(17)
			Isobutylene		(2, 18–21)
			Methacrylonitrile		(22)
			Methyl acrylate		(12)
			Methyl methacrylate		(13)
			Styrene		(13, 23–28)
			Tetranitromethane		(29)
Molecular weight	g mol^{-1}	Monomer	118.18		—
		Polymer range ($\overline{M}_w$)	$0.15–10 \times 10^5$		
Polydispersity	—	Depends on polymerization route	1.03–4.2		—
Infrared spectroscopy (peak positions)	cm^{-1}	Peak assignments			
		Aromatic ν_{CH}	3,100, 3,080, 3,040, 3,010		(30)
		Aromatic ν_{CH_3}	2,910		(30)
		Aromatic ν_{CH_2}	2,840		(30)
		Phenyl ring	1,495		(30)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Infrared spectroscopy (peak positions)	cm^{-1}	Peak assignments		
		δ_{CH_3}, δ_{CH_2}	1,430, 1,390	(30)
		Helical chain structure	1,363, 1,314, 1,290	(31)
		δ_{CH_3}	1,360	(30)
		Stereoregular chain structure	1,346, 1,093	(31)
		Chain conformational regularity	1,334, 1,304, 1,224, 1,191	(31)
		In-plane CH bending of phenyl ring	1,160, 1,090, 1,000	(30)
		Chain conformational regularity	977, 861, 749, 738	(31)
		Out-of-plane CH bending of phenyl ring	790	(30)
NMR spectroscopy		Measurement conditions		
		Cross-polarization/magic angle spinning		(32)
		15–20% (w/v) solution in $CDCl_3$ at 30°C		(22)
		Solution in CCl_4 at 75°C		(30)
		10% solution in $CDCl_3$ at 24°C		(33)
		^{1}H spin echo at 60 MHz of 10% (w/w) solution		(34)
		^{13}C at 25 MHz of 10% (w/v) solution in $CDCl_2$		(34)
		^{1}H and ^{13}C spectra in *o*-dichlorobenzene at 130°C		(31)
Thermal expansion coefficient α	K^{-1}	Below T_g	3.15×10^{-4}	(35)
		$150\,K < T < T_g$	7.1×10^{-5}	(36)
		Above T_g	6.31×10^{-4}	(35)
		$T_g < T < 440\,K$	16×10^{-5}	(36)
Density	$g\,cm^{-3}$	20°C	1.022	(35)
		23°C	1.016	(33, 37)
		25°C	1.011	(36)
Solvents	—	Strength		
		Good	Benzene	(38)
		Good	Butyl acetate	(38)
		—	Carbon tetrachloride	(30)
		Intermediate	Cyclohexane	(38, 39)
		Intermediate	Dichloroethane	(39)
		Theta	Diethyl succinate	(38, 39)
		Intermediate	Methyl ethyl ketone	(38, 39)
		—	Tetrahydrofuran	(30)
		Good	Toluene	(38–40)
Theta temperature	K	Solvent: diethyl succinate	289.4	(39)
Flory-Huggins interaction parameter χ	—	Volume fraction polymer in toluene at 22°C		(16)
		0.20	0.378	
		0.24	0.401	
		0.28	0.413	
		0.32	0.412	
		0.36	0.404	
		0.40	0.382	

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Flory-Huggins interaction parameter χ	–	Volume fraction polymer in toluene at 22°C			(16)
		0.44	0.364		
		0.48	0.356		
		0.52	0.355		
		0.56	0.352		
		0.60	0.341		
		0.64	0.322		
Mark-Houwink parameters: K and a	$K = \text{mol g}^{-1}$ a = None	$\overline{M}_w$ range = (20–155) $\times 10^4$	$K \times 10^5$	a	(41)
		Cyclohexane at 30°C	8.07	0.72	
		Methyl ethyl ketone at 30°C	10.3	0.68	
		Toluene at 30°C	6.88	0.76	
Second virial coefficient A_2	$\text{mol cm}^3\text{ g}^{-2}$	–	See table below		(39)
Mean square radius $\langle r^2\rangle$	cm^2	–	See table below		(39)
Intrinsic viscosity $[\eta]$	dl g^{-1}	–	See table below		(39)

Solvent	$\overline{M}_w \times 10^{-4}$	T (°C)	$A^2 \times 10^4$	$\langle r^2\rangle \times 10^{12}$	$[\eta]$
Cyclohexane	84.7	30	1.56	12.4	1.25
Dichloroethane	118	30	1.70	18.9	1.83
Diethyl succinate	197	60	0.58	23.9	1.34
		40	0.41	20.8	1.16
		20	0.09	17.0	0.89
		18	0.03	16.1	0.85
		16	−0.02	15.5	0.79
	89.6	60	0.81	11.5	1.05
		40	0.60	10.4	0.94
		20	0.20	8.85	0.75
		18	0.11	8.54	0.72
		16	0.00	8.00	0.69
	76.2	60	0.90	9.25	0.95
		40	0.70	8.55	0.85
		20	0.17	7.37	0.70
		18	0.12	6.94	0.67
		16	−0.01	6.50	0.64
	68.4	60	0.83	8.18	0.90
		40	0.61	7.55	0.79
		20	0.12	6.37	0.65
		18	0.06	6.15	0.62
		16	−0.04	5.85	0.60
Methyl ethyl ketone	121	30	1.00	17.3	1.40
Toluene	180	30	2.18	36.9	3.72
	81.3	30	3.08	15.4	2.20
	47.6	30	3.41	8.70	1.36
	19.2	30	4.37	3.00	0.73

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Poly(*p*-methylstyrene)

Crystalline unit cell[42]

Isomer	Lattice	Monomers per unit Cell	Cell dimensions (Å)			Cell angles		
			a	*b*	*c*	α	β	γ
Syndiotactic (>95%) Form III	*Pnam*	6	13.36	23.21	5.12	90	90	90

Crystalline polymorphs

Polymorph	Description	Reference
Syndiotactic Form I	Chains have helical s(2/1)2 conformation, repeat distance of 7.8 Å, $T_m = 178°C$	(43, 44)
Syndiotactic Form II	Chains have helical s(2/1)2 conformation, repeat distance of 7.8 Å, $T_m = 201°C$	(43, 44)
Syndiotactic Form III	Chains have *trans* planar conformation, repeat distance of 5.1 Å, $T_m = 224°C$	(43, 44)
Syndiotactic Form IV	Chains have *trans* planar conformation, repeat distance of 5.1 Å, $T_m = 194°C$	(43, 44)
Syndiotactic Form V	Chains have *trans* planar conformation, repeat distance of 5.1 Å	(44)
Syndiotactic clathrates	Chains have helical s(2/1)2 conformation, repeat distance of 7.8 Å	(43, 44)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Crystalline density	$g\,cm^{-3}$	25°C	1.00	(42)
Glass transition temperature T_g	K	–	356	(35)
		Creep tests	361	(45)
		Dynamic thermal analysis (DTA)	366	(46)
		Stress relaxation	366	(45)
		Differential scanning calorimetry (DSC)	374	(45)
		DSC	380	(47)
		DSC	383	(33)
		DSC	384	(48)
		DSC, extrapolated to $\overline{M}_w^{\infty}$	384	(30)
		Dynamic mechanical analysis (DMA)	385	(45)
		Dielectric analysis (DEA)	391	(45)
		T_g dependence on $\overline{M}_n$	$384-(2.56 \times 10^5)/\overline{M}_n$	(30)
Sub-T_g transitions	K	β transition, DMA at 1 Hz, $E_a = 71\,kJ\,mol^{-1}$	313	(45)
		γ transition, DMA at 1 Hz, $E_a = 29\,kJ\,mol^{-1}$	244	(45)
		δ transition, resonance electrostatic method at 9,700 Hz	92	(49)
Heat capacity C_p	$J\,mol^{-1}\,K^{-1}$	300 K to T_g	$-3.54 + 0.5138T$	(47)
		T_g to 500 K	$90.85 + 0.3564T$	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Deflection temperature	K	ASTM Test D-264 under 1.8 MPa load	365	(50)
Tensile modulus	MPa	ASTM Test D-638	2,206	(50)
Dynamic storage modulus	MPa	DMA, 1 Hz, 20°C	3,400	(45)
Dynamic loss modulus	MPa	DMA, 1 Hz, 20°C	640	(45)
Tensile strength	MPa	ASTM test D-638	49.6	(50)
Yield strain	%	ASTM test D-638	3.0	(50)
Flexural modulus	MPa	ASTM test D-790	2,992	(50)
Flexural strength	MPa	ASTM test D-790	79.3	(50)
Impact strength	$J m^{-1}$	ASTM test D-256, 73°C, notched 3.175-mm thick specimen	16	(50)
Hardness	80	ASTM test D-785, Rockwell M scale	80	(50)
Resonance frequency	Hz	Mechanical damping measurements of polymer disks	9,700	(49)
Index of refraction	–	20°C	1.5766	(35)
		20°C	1.58	(37)
Dielectric constant	–	Dielectric spectroscopy, 1 kHz and 23°C	2.86	(48)
		Dielectric spectroscopy, 1 kHz and 25°C	2.476	(36)
		Dielectric spectroscopy at 10 kHz, varies linearly with temperature		(51)
		−196°C	2.62	
		70°C	2.53	
Permeability coefficient *P*	$m^3(STP)m\ m^{-2}\ s^{-1}\ Pa^{-1}\ (\times 10^{-12})$	CH_4 at 1 atm and 35°C	2.29	(52)
		CO_2 at 1 atm and 35°C	39.6	(52)
		CO_2 at 200 mm Hg pressure and 25°C	12.0	(53)
		He at 1 atm and 35°C	49.3	(52)
		N_2 at 1 atm and 35°C	2.00	(52)
		O_2 at 1 atm and 35°C	9.6	(52)
		O_2 at 200 mm Hg pressure and 25°C	1.2	(53)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Diffusion coefficient D	$m^2 s^{-1}$ ($\times 10^{-12}$)	CH_4 at 1 atm and 35°C	4.0	(52)
		CO_2 at 1 atm and 35°C	13.7	(52)
		CO_2 at 200 mm Hg pressure and 25°C	5.8	(53)
		N_2 at 1 atm and 35°C	10.4	(52)
		O_2 at 1 atm and 35°C	28.1	(52)
		O_2 at 200 mm Hg pressure and 25°C	10.2	(53)
Degradation properties	Experimental conditions		Degradation	
	Irradiation with 284 nm UV photons		C–H cleavage, polymer degradation	(40)
	Isothermal treatments between 250 and 365°C		Weight loss between 1 and 75% due to random scission and depolymerization; above 330°C cross-linking occurs	(30)
Maximum thermal decomposition temperature	K	—	490	(54)
G value of scission	$mol\,J^{-1}$	γ radiation at 130°C	4.43×10^{-9}	(55)
G value of cross-linking	$mol\,J^{-1}$	γ radiation at 65°C	6.28×10^{-9}	(55)
		γ radiation at 98°C	2.27×10^{-9}	
G value of gas evolution $G(H)$	$mol\,J^{-1}$	γ radiation at −196°C	3.30×10^{-9}	(55)
		γ radiation at −80°C	3.71×10^{-9}	
		γ radiation at 25°C	4.43×10^{-9}	
		γ radiation at 65°C	4.84×10^{-9}	
		γ radiation at 130°C	6.18×10^{-9}	

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Poly(methyltrifluoropropylsiloxane)

MICHAEL J. OWEN

ACRONYMS, TRADE NAMES LS ''Low swell'', FS ''Fluorosilicone''

CLASS Polysiloxanes

STRUCTURE $[CH_3(CF_3CH_2CH_2)SiO]$

MAJOR APPLICATIONS Antifoam fluids, lubricants, protective gels, and elastomers and sealants in applications exposed to hydrocarbon fuels and oils and organic solvents in the automotive and aerospace industries. Longer fluorocarbon side-chain fluorosilicones are available with developing use as release coatings for silicone-based adhesives.

PROPERTIES OF SPECIAL INTEREST Excellent solvent resistance combined with good thermal stability. Widest hardness range and broadest operating service temperature range of any fuel resistant elastomer. General ease of fabrication. Retention of many properties (e.g., electrical) in harsh environments. Surface energy comparable to methylsiloxanes (higher liquid values, lower or similar solid values). More highly fluorinated fluorosilicones have significantly lower surface energy.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	MW = 14,000	1.30	(1)
		25°C	1.292	(2)
Solubility parameter	$(MPa)^{1/2}$	Not given	17.88	(2)
Theta temperatures	K	Cyclohexyl acetate	298	(3)
		Methyl hexanoate	345.8	
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None	Methyl hexanoate, 72.8°C	$K = 4.45 \times 10^{-4}$, $a = 0.50$	(3)
		Cyclohexyl acetate, 25°C	$K = 4.10 \times 10^{-4}$, $a = 0.50$	
		Ethyl acetate, 25°C	$K = 5.92 \times 10^{-5}$, $a = 0.70$	
Glass transition temperature	K	Atactic, DSC	203	(4)
		Made from *trans* trimer isomer (100%), DSC	204.2	(5)
		Made from *cis* trimer isomer (96%), DSC	207.2	(5)
Melting temperature	K	Made from *trans* trimer isomer (100%), DSC	268.6	(5)
		Made from *cis* trimer isomer (96%), DSC	321	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength	MPa	Range for typical filled commercial elastomers		(6)
		22°C	5.5–11.7	
		204°C	2.4–4.1	
Maximum extensibility	%	Range for typical filled commercial elastomers		(6)
		22°C	100–600	
		204°C	90–300	
Index of refraction	–	MW = 14,000	1.383	(1)
Dielectric constant	–	100 Hz	6.85	(7)
Loss factor	–	100 Hz	0.109	(7)
Surface tension	$mN\,m^{-1}$	Liquid, 25°C, ''infinite'' MW	24.4	(8)
		Solid, Owens and Wendt method	13.6	(9)
		Critical surface tension of wetting	21.4	(9)
Permeability coefficient	$m^3(STP)\,m\,s^{-1}\,m^{-2}\,Pa^{-1}$	He, 100 psi, 35°C	1.85×10^{-15}	(4)
		O_2, 100 psi, 35°C	1.63×10^{-15}	
		CO_2, 100 psi, 35°C	1.04×10^{-14}	
		CH_4, 100 psi, 35°C	1.51×10^{-15}	

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Poly(norbornene)

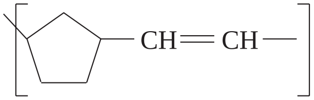
VASSILIOS GALIATSATOS

ALTERNATIVE NAME, TRADE NAMES Poly(1,3-cyclopentylenevinylene), Norsorex®, Telene (copolymer)

CLASS Diene elastomers

MAJOR APPLICATIONS The rubbery polymers are useful as vibration and noise damping materials. Also for oil spill recovery, sound barrier materials, and for soft seals and gaskets.

STRUCTURE



PREPARATION The polymer obtained by ring-opening polymerization of norbornene. Both *cis* and *trans* structures may result. Polymer is typically free of oligomers and macrocycles. Cross-linking can occur by conventional accelerated sulfur vulcanization.[1,2]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Typical molecular weight of polymer	$g\ mol^{-1}$	–	$2\text{–}3 \times 10^6$	–
Typical appearance	–	–	White powder	–
Glass transitions temperature T_g	K	Commercial product Incorporation of a mineral oil extender, which gives useful rubbery properties, including very soft compositions 20% *cis* content polymer, which is totally amorphous	308–318 228–213 308	(3)
Crystalline melting temperature	K	Hydrogenated polynorbornene	413.8	(3)
Heat of fusion	$kJ\ g^{-1}$	Hydrogenated polynorbornene	58.7×10^{-3}	(3)
Decomposition temperature	K	–	>673	(3)
Density	$g\ cm^{-3}$	–	0.30	(3)
Index of refraction	–	–	1.534	(3)
Hardness	Shore A	Cured for 10 min at 320°F	40	(3)
100% modulus	MPa	Cured for 10 min at 320°F	0.552	(3)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
300% modulus	MPa	Cured for 10 min at 320°F	2.24	(3)
Tensile strength	MPa	Cured for 10 min at 320°F	15.1	(3)
Elongation	%	Cured for 10 min at 320°F	560	(3)
FTIR spectrum	cm^{-1}	*Cis* absorption *Trans* out of plane =C−H bending *Cis* in plane =C−H bending	740 960 1,404	(4)
Supercritical fluid behavior	Polynorbornene, molecular weight = 2×10^6, 25°C, pressure = 19.0 MPa			—

Force field parameters for bond stretching[5]

Bond	Bond length (Å)	Force constant (kJ $Å^{-1}$)
C2-C3	1.551	2,358
C1-C2	1.560	2,975
C1-C&	1.545	3,050
CH (averaged)	1.086	3,248

Force field for angle bending[5]

Angle	Angle (degrees)	Force constant (kJ $Å^{-2}$)
(C7)H2	109.4	565
(C1-6)H2	107.8	573
C1-C7-C4	96.1	688
C2-C1-C6	108.3	1122
C2-C1-C7	101.6	426
C1-C2-C3	103.2	506

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Characteristic ratio	—	Calculated —	12.1 11.4	(5)
Entanglement molecular weight	$g\ mol^{-1}$	—	41,000	(5)
Van der Waals volume	$cm^3\ mol^{-1}$	Calculated Experimental	108 149.9	(5)
Intrinsic viscosity	$dl\ g^{-1}$	In benzene at 30°C (at a strain rate = 100% min^{-1} at 25°C)	3.4, 4.3, 5.0, 9.0	(6)

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Poly(norbornene)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Trans/cis	—	Deduced from the ratio of optical ratios at 10.35 and 13.8 μm (at a strain rate = 100% min^{-1} at 25°C)	3, 4, 4.2, 4.3	(6)
Tensile strength	psi ($\times 10^3$)	At a strain rate = 100% min^{-1} at 25°C	3, 4.2, 4.8, 6.5	(6)
Ultimate elongation	%	At a strain rate = 100% min^{-1} at 25°C	16, 80, 85, 300	(6)
Young's modulus	MPa	At a strain rate = 100% min^{-1} at 25°C	90, 70, 50, 20	(6)
Crystallographic identity period		2 repeat units per unit cell, 1.18 nm		(7)

Suppliers

Trade name	Supplier
Norsorex	Atochem North America, Inc., Philadelphia, Pennsylvania, USA Atochem Deutschland GmbH, Düsseldorf, Germany
Telene (copolymer)	BF Goodrich Company, Specialty Polymers Division, Brecksville, Ohio, USA

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Polyoctenamer

VASSILIOS GALIATSATOS

ACRONYM, ALTERNATIVE NAME, TRADE NAME TOR, poly(1-octenylene), Vestenamer (Hüls)

CLASS Diene elastomers

STRUCTURE $(CH{=}CH(CH_2)_6)_n$

SYNTHESIS Ring-opening polymerization of cyclooctene in the presence of Ziegler-Natta catalysts.

FRACTIONATION METHODS Gel permeation chromatography employing THF as a solvent.[1]

PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Molar absorptivities of IR bands attributed to *trans* and *cis* units	$(\text{mol cm})^{1}$	ε_{trans} (10.35 μm) ε_{cis} (7.12 μm)			135 8.7	(2)
Mark-Houwink parameters: K and a	$K = \text{ml g}^{-1}$ a = None	40–50% *trans* content at 30°C in toluene			$K = 8.0 \times 10^4$ $a = 0.63$	(3)
Glass transition temperature	K	*Cis*-polyoctenamer, DSC			165	(4)
Crystalline melting temperatures T_m	K	*Trans* %	DH (J g^{1})	Technique		
		290	DSC	–	37.6	(5)
		75–85	–	X-ray	335, 340	(6)
		100 (extrapolated)	220.1	Diluent	350	(7)
		100 (extrapolated)	136.4	Dilatometry	346	(8)
		100 (extrapolated)	185.8	Diluent	333	(8)
Crystallographic information	Monoclinic, 1 repeat unit in unit cell, 0.99 nm identity period					(9)
	Triclinic, 1 repeat unit in unit cell, 0.97 nm identity period					(10)

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Polypentenamer

VASSILIOS GALIATSATOS

ALTERNATIVE NAME Poly(1-pentenylene)

CLASS Diene elastomers

STRUCTURE $(CH{=}CH(CH_2)_3)_n$

SYNTHESIS Ring-opening polymerization of cyclopentene. *Trans*-polypentenamer is produced by Ziegler-Natta polymerization employing a catalyst based on aluminum triethyl/tungsten hexachloride compound. Aluminum diethylchloride/ molybdenum pentachloride compounds may be employed to produce the *cis* isomer. Both macrocycles and linear chains are produced during polymerization.

FRACTIONATION METHODS Fractional precipitation in toluene/methanol (solvent/nonsolvent) mixtures at 40/20°C.[1,2]

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Gel permeation chromatography	—	Using THF as the solvent	—		(3)
Molar absorptivities of IR bands attributed to *trans* and *cis* units	$(\text{mol cm})^{-1}$	ε_{trans} (10.35 μm)	152		(4)
		ε_{cis} (7.12 μm)	5.0		
Mark-Houwnink parameters: K and a	$K = \text{ml g}^{-1}$	*Trans*-polypentenamer			(5)
	a = None	(~85% *trans* content)	$K \times 10^4$	a	
		Toluene, 30°C	5.21	0.69	
		Cyclohexane, 30°C	5.69	0.68	
		i-Amyl acetate (θ solvent), 38°C	23.4	0.63	
Specific refractive index increment	—	*n*-Hexane (dilute solution at 25°C)			(6)
		436 nm	0.175		
		546 nm	0.171		
Glass transition temperature T_g	K	*Cis*-polypentenamer	159		(7)
		DTA	163		(8)
		TBA			
		Trans-polypentenamer			
		DTA	176		(9)
		DTA	183		(10)
		DSC	178		(11)
		TBA	180		(8)
		DSC	182		(12)

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Crystalline melting temperature T_m	K	*Trans* (%)	ΔH (J g^{-1})	Technique		
		1	–	DTA	232	(7)
		85	–	DTA	291	(9)
		100 (extrapolated)	Diluent	176.6	–	(13)
		100 (extrapolated)	–	DSC	317	(12)
Effect of microstructure on crystallization rate of *trans*-polypentenamer ($T_{1/2}$)	hours	*Trans* (%) at 0°C				(14)
		93 (85 based on IR analysis)			0.3	
		90 (82 based on IR analysis)			0.8	
		89 (81 based on IR analysis)			13	
		87 (79 based on IR analysis)			45	
Crystallographic information	Orthorhombic, 2 repeat units in unit cell, 1.19 nm identity period					(15)
Unperturbed dimensions $r_0/M^{1/2}$	nm	At 38°C, utilizing the Flory-Fox theory of viscosity vs. molecular weight in a θ solvent			9.91×10^6	–
Relaxation behavior	K	By DMA, for 82% *trans* content ($M_n = 94{,}400\ g\ mol^{-1}$, $M_w = 172{,}300\ g\ mol^{-1}$) at 110 Hz				–
		α relaxation			353	
		β relaxation			273	
		γ relaxation			158, 153	

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Poly(1,4-phenylene)

JACEK SWIATKIEWICZ AND PARAS N. PRASAD

ACRONYM, ALTERNATIVE NAME PPP, poly(*p*-phenylene)

CLASS Polyaromatics

STRUCTURE $[-C_6H_4-]$

PROPERTIES OF SPECIAL INTEREST Electroactive and electroluminescent material. Electrical properties can be tuned by choice of doping and preparation procedure. Insoluble and infusible material, sustains high-temperature treatment.

PREPARATIVE TECHNIQUES Various aryl coupling reactions, pyrolysis of the polymer precursors, anodic polymerization.[1–4]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	Amorphous	1.11 ± 0.02	(3)
		Semi-crystalline	1.228	(3)
		Highly crystalline, annealed	1.39	(2)

Unit cell dimensions

Lattice	Monomers per unit cell	Cell dimensions (nm)			Cell angles			Reference
		a	*b*	*c*	α	β	γ	
Monoclinic	2	0.779	0.562	0.426	–	79°	–	(2)
Monoclinic	2	0.806	0.555	0.430	–	100°	–	(5)
Orthorhombic	2	0.781	0.553	0.420	–	–	–	(5)
Orthorhombic	2	0.780	0.556	0.420	–	–	–	(5)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
IR (characteristic absorption frequencies)	cm^{-1}	–	3,027	(3)
			3,030	(4, 6)
			1,603	(3)
			1,600	(4, 6)
			1,482	(3)
			1,460	(4, 6)
			1,003	(3)
			1,000	(4, 6)
			808	(3)
			803	(4, 6)
			765	(3)
			760	(4, 6)
			509	(3)
			500	(4, 6)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Raman (characteristic frequencies)	cm^{-1}	–	1,600	(7)
			1,598	(8)
			1,280	(7)
			1,276	(8)
			1,220	(7, 8)
Wavelength at maximum of the band	nm	UV-Vis absorption	362	(2)
			333–338	(3)
			350	(9)
		Photo-excitation	400	(9)
Emission band	nm	Photo-luminescence	500	(9)
			460	(10)
Electronic conductivity	$S\,cm^{-1}$	$T = 298\,K$	1.6×10^{-13}	(11)
			3.3×10^{-13}	(9)
Energy gap	eV	–	2.7	(10)
			2.8	(12)
Electroluminescence emission peak	nm	–	460	(10)

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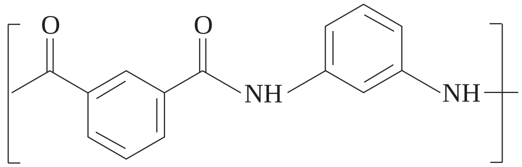
Poly(*m*-phenylene isophthalamide)

ZHENGCAI PU

TRADE NAMES Nomex, Teijinconex, Fenilin

CLASS Aromatic polyamides

STRUCTURE[1]



MAJOR APPLICATIONS Heat-resistant and flame-retardant apparel; (high-voltage) electrical insulation; low-, medium-, and high-density pressboard; honeycomb structure composite.

PROPERTIES OF SPECIAL INTEREST High extensibility relative to other aromatic polyamide, high degradation and glass transition temperature, excellent dielectric property, and good spinnability.

PRODUCERS AND/OR SUPPLIERS Du Pont (Nomex); Teijin Ltd., Japan (Teijinconex); Russia (Fenilin)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Anistropy of segment	cm^{-3}	Sulfuric acid		(2)
		$\alpha_1 - \alpha_2$	3.6×10^{23}	
		$\alpha_{\|\|} - a_{\perp}$	1.0×10^{23}	
Coefficient of linear thermal expansion	K^{-1}	294–477 K	6.2×10^{6}	(3)
Solvents	Concentrated sulfuric acid, methanesulfonic acid, dimethyl acetamide, dimethylsulfoxide, DMF, N-methylpyrrolidone			(3)
Nonsolvents	Hexamethylphosphoramide, *m*-cresol, formic acid			(3)
Density ρ	$g\ cm^{-3}$	–	1.38	(3, 4)
Dielectric constant	–	60 Hz	1.6–2.9	(3)
Dielectric loss	–	60 Hz, 50% relative humidity	0.006	(3)
Dielectric strength	$kV\ m^{-1}$	23°C, 50% relative humidity	2.0–3.9 $(\times 10^4)$	(3)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Diffusion coefficient	$m^2\ s^{-1}$	$M_w = 4.3$–$112\ kg\ mol^{-1}$, 3% LiCl in DMF, 298 K	6.19–0.82 ($\times 10^{11}$)	(2)
Glass transition temperature	K	Heating rate $= 2\ K\ min^{-1}$	553	(2, 3, 5)
Heat capacity	$kJ\ K^{-1}\ mol^{-1}$	–	0.29	(3)
Inherent viscosity η_{inh}	$dl\ g^{-1}$	30°C, in 0.5 g fiber/100 ml sulfuric acid solution	1.86–2.11	(6)
Limiting oxygen index (LOI)	%	–	28	(3, 4, 7)
Mark-Houwink parameters: K and a	$K = ml\ g^{-1}$ $a =$ None	–	$K = 3.7 \times 10^{-4}$ $a = 0.73$	(3)
Melting point	K	DTA transition	708	(3, 5)
Initial tension modulus	MPa	–	1.37×10^4	(8)
Flexure modulus	MPa	3.2 mm thick pressboard	2.55–3.60	(3)
Dynamic storage modulus	MPa	10% fiber in DMAc/LiCl, $\omega = 1\ s^{-1}$	2×10^5	(3)
Refractive index increment dn/dc	$ml\ g^{-1}$	DMA DMA + LiCl room temperature, $\lambda_0 = 546\ nm$	0.245 0.219–0.200	(2)

Resistance to chemicals[(3)]

Chemical	Effect on breaking strength					
	None			Appreciable		
	Conc. (%)	Temp. (K)	Time (h)	Conc. (%)	Temp. (K)	Time (h)
Hydrochloric acid	35	294	10	10	368	8
Nitric acid	10	294	100	70	294	100
Sulfuric acid	10	294	100	70	368	8
Acetic acid	100	294–366	10–1,000	–	–	–
Benzenesulfonic acid	–	–	–	100	366	10
Formic acid	91	294	1,000	–	–	–
Ammonium hydroxide	28	294	100	–	–	–
Sodium hydroxide	10	294	100	50	333	100
Acetone	100	294	1,000	–	–	–
Benzene	100	294	1,000	–	–	–
m-Cresol	100	294	1,000	–	–	–
Ethyl alcohol	100	294	1,000	–	–	–
Gasoline (leaded)	100	294	1,000	–	–	–
Nitrobenzene	100	294	1,000	–	–	–
m-Xylene	100	343	168	–	–	–

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Resistance to radiation (β-ray)*[(3)]

Dose† (Mgrads)	Retained tensile strength (%)	Retained elongation (%)	Dielectric strength ($kV\,m^{-1}$)	Dielectric constant‡	Dissipation factor‡
0	100	100	3.4×10^4	3.1–2.9	0.0083–0.0183
100	100	92	3.4×10^4	3.0–2.9	0.0135–0.0205
200	99	91	3.3×10^4	3.0–2.9	0.0104–0.0198
400	99	88	3.3×10^4	3.0–2.9	0.0120–0.0199
800	97	82	3.3×10^4	3.0–2.8	0.0089–0.0185
1,600	86	47	3.4×10^4	3.1–3.0	0.0137–0.0195
3,200	81	27	3.5×10^4	2.3–2.2	0.0071–0.0148
6,400	69	16	3.1×10^4	2.5–2.4	0.0095–0.0174

*0.25 mm Nomex Type 410 paper, cross direction.
†2 MeV electrons.
‡60 Hz to 10 kHz.

Resistance to radiation (X-ray)[(3)]

X-ray (kV)	Irradiation time (h)	Breaking strength retained (%)
50	50	85
50	100	73
50	250	49

Resistance to temperature[(3)]

Temperature (K)	Breaking tenacity (MPa)	Initial modulus (MPa)	Breaking elongation (%)
223	738	1.76×10^4	19.4
311	614	1.46×10^4	21.3
422	521	1.15×10^4	23.7
533	346	0.80×10^4	26.0

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Resistivity	ohm cm	50% relative humidity	1016	(3)
Secondary-relaxation	K	Torsion pendulum, 1 Hz		(7)
		T_b	550	
		T_g	352	
Temperature	K	Begin to degrade	573	(3)
		10% weight loss	731	
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	—	0.13	(3)
Tenacity at break	N/tex	—	0.39–0.49	(6)
Tensile strength at break	MPa	—	54–68	(6)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Elongation at break	%	—	20–30	(3, 6, 9)
Flexure strength	MPa	3.2 mm thick pressboard	0.08–0.09	(3)
Shear strength	N	—	31,000	(3)
Upper use temperature	K	In air	643	(10)
Upper use voltage	$kV\ m^{-1}$	23°C, 50% relative humidity	1.6×10^3	(3)
Water uptake	% (w/w)	20°C, 65% relative humidity	6.5–9.3	(6, 11)
Zero-strength temperature	K	—	713	(12)

Sedimentation coefficient at zero concentration[2]

Solvent	Temperature (K)	M_w ($kg\ mol^{-1}$)	S_0 (s)
DMF	298	30.2–156	$(1.9 \times 10^{15})M^{0.44}$
LiCl ($2.5\ g\ l^{-1}$ + 96% H_2SO_4) in DMF	298	20.7–142	$(2.8 \times 10^{15})M^{0.39}$
3% LiCl in DMF	298	4.3–112	0.33–1.15($\times 10^{13}$)

Unit cell data

Crystallographic system	Triclinic[3]	Ortho[2]	Ortho[2]
Space group	$P1–C_1^1$	—	—
Cell dimension			
a_0 (Å)	5.27	6.7	5.1
b_0 (Å)	5.25	4.71	5.0
c_0 (Å)	11.3	11.0	23.2
α (°)	111.5	—	—
β (°)	111.4	—	—
γ (°)	88	—	—
Repeat unit per unit cell	1	1	2

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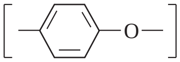
Poly(*p*-phenylene oxide)

ALLAN S. HAY AND YONG DING

ACRONYMS PPO, PPE

CLASS Polyether thermoplastics

STRUCTURE



PROPERTIES OF SPECIAL INTEREST Highly crystalline polymer, excellent chemical and solvent resistance. Not commercially available.

PREPARATIVE TECHNIQUES Poly(*p*-phenylene oxide) is prepared from mono *p*-bromo- or *p*-chloro-phenolate at 170–200°C in the presence of cuprous salt as catalyst.[1–3]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight of repeat unit	$g\,mol^{-1}$	–	92.03	–
IR (characteristic absorption frequencies)				(3)
Thermal expansion coefficients	K^{-1}	Amorphous sample, DSC		(4)
		Above T_g	249×10^{-6}	
		Below T_g	62×10^{-6}	
		Crystalline sample, DSC		(4)
		$0.7T_m < T < 0.95T_m$	93×10^{-6}	
Density (amorphous)	$g\,cm^{-3}$	–	1.27	(5)
Solvents	Boiling nitrobenzene, benzophenone, diphenyl ether, N-methylpyrrolidinone, tetralin, naphthalene, and hexamethylphosphoric acid triamide			(3)
Nonsolvents	Room temperature: acetone, alcohols, tetrahydrofuran, halogenated solvents			(3)
Lattice	–	–	ORTH	(5)
Space group	–	–	*Pbcn*	(5)
Chain conformation	–	–	7 * 2/1	(5)
Unit cell dimensions	Å	Compression-molded or uniaxially oriented	$a = 8.07$ $b = 5.54$ $c = 9.72$	(5)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Unit cell contents (number of repeat units)			4	(5)
Degree of crystallinity*	%	Hold at 230°C for 1 h, cooling rate > 1,000°C min^{-1}, x-ray	0	(4)
		Hold at 230°C for 1 h, cooling rate 100°C min^{-1}, x-ray	42	
		Hold at 230°C for 1 h, cooling rate 1°C min^{-1}, x-ray	45	
		Hold at 230°C for 1 h, cooling rate 0.1°C min^{-1}, x-ray	70	
		Hold at 112°C for 1 h, cooling rate 0.1°C min^{-1}, x-ray	58	
		25°C, 0.2% nitrobenzene solution quenched with alcohol, x-ray	15	
Heat of fusion (of repeat units)	kJ mol^{-1}	DSC	7.835 ± 0.419	(4)
Entropy of fusion (of repeat units)	kJ K^{-1} mol^{-1}	DSC	0.015 ± 0.003	(4)
Density (crystalline)	g cm^{-3}	–	1.407 ± 0.01	(5)
Glass transition temperature	K	DSC	363	(4)
Melting point	K	DSC	535 ± 10	(4)
Heat capacity (of repeat units)	kJ K^{-1} mol^{-1}	300–358 K	$C_p = (0.337T + 7.95) \times 10^{-3}$	
		358–620 K	$C_p = (0.1425T + 99.01) \times 10^{-3}$	(6)
Dielectric constant ε'	–	100 Hz, 296 K	4.76	(2)
		100 Hz, 348 K	4.72	
		100 Hz, 398 K	4.73	
		100 Hz, 448 K	4.76	
		100 Hz, 498 K	4.60	
		100 Hz, 523 K	4.59	
		100 Hz, 548 K	4.78	
		100 Hz, 573 K	7.01	
		1000 Hz, 296 K	4.76	
		1000 Hz, 348 K	4.71	
		1000 Hz, 398 K	4.71	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
		1000 Hz, 448 K	4.75	
		1000 Hz, 498 K	4.58	
		1000 Hz, 523 K	4.53	
		1000 Hz, 548 K	4.50	
		1000 Hz, 573 K	4.51	
		1×10^5 Hz, 296 K	4.76	
		1×10^5 Hz, 348 K	4.71	
		1×10^5 Hz, 398 K	4.68	
		1×10^5 Hz, 448 K	4.71	
		1×10^5 Hz, 498 K	4.54	
		1×10^5 Hz, 523 K	4.50	
		1×10^5 Hz, 548 K	4.47	
		1×10^5 Hz, 573 K	4.42	
Dielectric loss ε''	–	100 Hz, 296 K	0.0005	(2)
		100 Hz, 348 K	0.0005	
		100 Hz, 398 K	0.0047	
		100 Hz, 448 K	0.0079	
		100 Hz, 498 K	0.0311	
		100 Hz, 523 K	0.1745	
		100 Hz, 548 K	0.4417	
		100 Hz, 573 K	1.2085	
		1000 Hz, 296 K	0.0005	
		1000 Hz, 348 K	0.0007	
		1000 Hz, 398 K	0.0024	
		1000 Hz, 448 K	0.0027	
		1000 Hz, 498 K	0.0051	
		1000 Hz, 523 K	0.0180	
		1000 Hz, 548 K	0.0462	
		1000 Hz, 573 K	0.1876	
		1×10^5 Hz, 296 K	0.0013	
		1×10^5 Hz, 348 K	0.0006	
		1×10^5 Hz, 398 K	0.0016	
		1×10^5 Hz, 448 K	0.0027	
		1×10^5 Hz, 498 K	0.0092	
		1×10^5 Hz, 523 K	0.0023	
		1×10^5 Hz, 548 K	0.0023	
		1×10^5 Hz, 573 K	0.0026	

*Sample thickness: ca. 10 μm.

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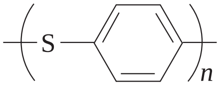
Poly(*p*-phenylene sulfide)

JUNZO MASAMOTO

ACRONYM, TRADE NAMES PPS, Ryton, Fortron, Torelina, Tohprene, DIC-PPS

CLASS Polysulfides

STRUCTURE



MAJOR APPLICATIONS Poly(*p*-phenylene sulfide) (PPS) is mainly used in the reinforced form with glass fiber or mineral fillers as a high-performance thermoplastic. It is used for electrical and electronic parts (e.g., plugs and multipoint connectors, bobbins, relays, switches, encapsulation of electronic component, etc.), automobile parts (air intake systems, pumps, valves, gaskets, components for exhaust gas recirculation systems, etc.), and as components for mechanical and precision engineering. Nonfiller PPS is used for fiber, film, sheet, nonwoven fabric, etc.

PROPERTIES OF SPECIAL INTEREST PPS is a semicrystalline thermoplastic. PPS reinforced with glass fiber or mineral fillers shows excellent mechanical properties, high thermal stability, excellent chemical resistance, excellent flame retardance, good electrical and electronic properties, and good mold precision. Recently developed linear type PPS additionally shows improved properties of elongation and toughness and opens the new route for the use of a neat polymer.

PREPARATIVE TECHNIQUE Condensation polymerization: Reaction between *p*-dichlorobenzene and sodium sulfide is accomplished in the presence of a polar solvent (e.g., N-methyl pyroridone). Polymer formation is accompanied by the production of sodium chloride as a byproduct. Medium-low molecular weight solid PPS powder is heated to below its melting point (448–553 K) in the presence of air. Several important properties of PPS change when the polymer is cured: (1) molecular weight increased; (2) toughness increased; (3) melt viscosity increased; (4) the color of the polymer changes from off-white to tan/brown. Modified high molecular weight linear polymer is directly obtained during polymerization by Phillips Petroleum using alkali metal carboxylate as a polymerization modifier. Kureha Chemical developed a modified process for obtaining linear type PPS, adding water during the last stage of polymerization.[1,2]

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	109	–
Typical molecular weight range of polymer	$g\,mol^{-1}$	Dilute solution light scattering and gel permeation chromatographic studies (performed in 1-chloronaphthalene at 220°C), and the inherent viscosity (performed in 1-chloronaphthalene at 206°C) is 0.16. The polymer is as polymerized, just before the curing step	18,000	(6, 7)
		The linear type of modified high molecular weight PPS by the Phillips modified process	35,000	(6)
Typical polydispersity index (M_w/M_n)	–	–	1.7	(8–10)
IR (characteristic absorption frequencies)	cm^{-1}	Skeletal benzene	480	(11, 12)
		Skeletal benzene	556	
		Skeletal benzene	724	
		Out-of-plane C–H bending	818	
		Out-of-plane C–H bending	960	
		Skeletal benzene	1,011	
		Phenylene sulfur stretching	1,096	
		In-plane C–H bending	1,178	
		In-plane C–H bending	1,235	
		Skeletal benzene	1,390	
		Skeletal benzene	1,471	
		Skeletal benzene	1,571	
		Skeletal benzene	1,652	
		Skeletal benzene	1,906	
		Skeletal benzene	2,299	
		C–H stretching	3,065	
Thermal expansion coefficients	K^{-1}	Unfilled	4.9×10^5	(10)
		40 wt% glass fiber-filled	4×10^5	
		Glass fiber and mineral-filled	2.8×10^5	
Solvents	–	>200°C	1-Chloronaphthalene	(1)
		>200°C	Biphenyl, 3-chlorobiphenyl, *o*-terphenyl	(13)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Nonsolvents	–	<200°C	Almost insoluble in organic and inorganic solvents	(10)
Mark-Houwink parameter: K and a	$K = \text{ml g}^{-1}$ a = None	1-Chloronaphthalene, at 208°C	$K = 8.91 \times 10^{-5}$ $a = 0.747$	(14)
Lattice	–	–	Orthorhombic	(15, 16)
Space group	–	–	D2H-14	(15, 16)
Chain conformation	All *trans* conformation defined by the plane of the C–S–C linkages (C–S–C bond angle 110°), while the phenyl rings are successively inclined at + and −45° to the plane.			–
	All *trans* conformation defined by the plane of the C–S–C linkages (C–S–C bond angle 103–107°), while alternate phenyl rings are nearly coplanar with the C–S–C plane, and while the remaining ones are inclined to 60°C.			(17)
Unit cell dimensions	Å	–	$a = 8.67$, $b = 5.61$, $c = 10.26$ (fiber identity period)	(15)
			$a = 8.68$, $b = 5.61$, $c = 10.26$ (fiber identity period)	(16)
Unit cell contents	Monomeric units	–	4	(15, 16)
Degree of crystallinity	%	X-ray diffraction method for fully crystalline PPS	65	(18)
Heat of fusion	kJ mol^{-1}	Typical heat of fusion of crystalline PPS	4.6–5.5	(19)
		100% crystalline material, by extrapolation	8.7	(16, 18)
Density	g cm^{-3}	Theoretical density for PPS crystalline	1.440 1.425	(15) (16)
		Observed density		(20)
		For PPS neat	1.35	
		40% glass reinforced	1.6	
		Glass and mineral filled	1.6–1.8	
Glass transition temperature	K	DSC	358	(2)
		M_w = 51,000, DSC, heating rate = 20°C min^{-1}	357	(16)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melting point	K	DSC	558	(2)
			568	(15)
		Equilibrium melting temperature, DSC determined from the relationships between T_m and T_c, 5°C min^{-1}		(21)
		$M_w = 15{,}000$	576	
		$M_w = 51{,}000$	588	
Heat capacity	$kJ\,K^{-1}\,mol^{-1}$	Unfilled, cured feed stock	0.112	(10)
Deflection temperature	K	Unfilled, cured feed stock, sample annealed at 260°C for 4 h, ASTM D648	408	(20)
		40% glass fiber reinforced PPS	>533	(20)
		Glass and mineral filled PPS	>533	(20)
		Unfilled, linear type PPS, ASTM D648 at 1.82 MPa	388	(22)
		40% glass fiber reinforced linear type PPS	538	(22)
		Glass and mineral filled linear type PPS	538	(22)
Tensile modulus	MPa	Biaxally oriented PPS film	2,600–3,900	(6)
		PPS fiber, draw ratio 3.8, 25.5 tex	3,500–4,700	
Tensile strength	MPa	Unfilled, cured feed stock, ASTM D638	65	(20)
		40% glass fiber reinforced	120	(20)
		Glass and mineral filled PPS	74	(20)
		Unfilled, linear type, ASTM D638	86	(22)
		40% glass fiber reinforced linear type	172	(22)
		Glass and mineral filled linear type	113	(22)
		Biaxially oriented PPS film	125–190	(6)
		PPS fiber, draw ratio 3.8, 25.5 tex	300	(6)
		PPS fiber	480	(22)
Yield stress	MPa	Unfilled, linear type	80	(23)
Yield strain $(L/L_0)_y$	%	Unfilled, linear type	5	(23)
Maximum extensibility	%	Unfilled, cured feed stock, ASTM D638	1.6	(20)
		40% glass fiber reinforced	1.2	(20)
		Glass and mineral filled	0.54	(20)
		Unfilled, linear type	12	(23)
		Unfilled, cured feed stock	2	(23)
		Unfilled, linear type, ASTM D638	3–6	(19)
		40% glass fiber reinforced linear type	1.7	(19)
		Glass and mineral filled linear type	1.0	(19)
		Unfilled, cured PPS	1.1	(6)
		Unfilled, linear type	21	(6)
		40% glass fiber reinforced cured PPS	0.5	(6)
		40% glass fiber reinforced linear type PPS	0.8	(6)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Maximum extensibility	%	Biaxially oriented PPS film	40–70	(6)
		PPS fiber, draw ratio 3.8, 25.5 tex	25–35	(6)
		PPS fiber	25–40	(22)
Flexural modulus	MPa	Unfilled, cured feed stock	3,860	(20)
		40% glass fiber reinforced	11,700	(20)
		Glass and mineral filled	15,200	(20)
		Unfilled, linear type	3,400	(23)
		Unfilled, linear type, ASTM D790	4,130	(22)
		40% glass fiber reinforced linear type	13,100	(22)
		Glass and mineral filled linear type	16,500	(22)
		Unfilled, cured PPS	3,845	(6)
		Unfilled, linear type	3,4041	(6)
		40% glass fiber reinforced cured PPS	1,5001	(6)
		40% glass fiber reinforced linear type PPS	1,800	(6)
Flexural strength	MPa	Unfilled, cured feed stock	96	(20)
		40% glass fiber reinforced	180	(20)
		Glass and mineral filled	100	(20)
		Unfilled, linear type	110	(23)
		Unfilled, linear type, ASTM D790	145	(22)
		40% glass fiber reinforced linear type	241	(22)
		Glass and mineral filled linear type	182	(22)
		Unfilled, cured PPS	104	(6)
		Unfilled, linear type	147	(6)
		40% glass fiber reinforced cured PPS	153	(6)
		40% glass fiber reinforced linear type	180	(6)
Impact strength, notched	$J\ m^{-1}$	ASTM D256		
		Unfilled, cured feed stock	16	(20)
		40% glass fiber reinforced PPS	69	(20)
		Glass and mineral filled	32	(20)
		Unfilled, linear type, ASTM D256	26	(20)
		40% glass fiber reinforced linear type	85	(22)
		Glass and mineral filled linear type	64	(22)
		Unfilled, cured PPS	10.7	(6)
		Unfilled, linear type	16.7	(6)
		40% glass fiber reinforced cured PPS	48.2	(6)
		40% glass fiber reinforced linear type	58.9	(6)
		Elastomer toughened PPS	500	(24)
		40% glass fiber reinforced elastomer toughened PPS	220	(24)
Impact strength, unnotched	$J\ m^{-1}$	ASTM D256		
		Unfilled, cured feed stock	101	(20)
		40% glass fiber reinforced PPS	240	(20)
		Glass and mineral filled	101	(20)
		Unfilled, linear type	900	(23)
		Unfilled, cured feed stock	60	(23)
		Unfilled, linear type	320–640	(23)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Impact strength, unnotched	$J\ m^{-1}$	40% glass fiber reinforced linear type	590	(23)
		Glass and mineral filled linear type	250	(23)
		Unfilled, cured PPS	80.3	(6)
		Unfilled, linear type	578	(6)
		40% glass fiber reinforced cured PPS	139	(6)
		40% glass fiber reinforced linear type	241	(6)
Compressive strength	MPa	Unfilled, cured feed stock	110	(20)
		40% glass fiber reinforced PPS	145	
		Glass and mineral filled	110	
Rockwell hardness	–	Unfilled, cured feedstock	R-120	(20)
		40% glass fiber reinforced PPS	R-123	
		Glass and mineral filled	R-121	
Entanglement molecular weight	$g\ mol^{-1}$	–	20,000	(8)
Dielectric strength	$kV\ mm^{-1}$	40% glass fiber filled, ASTM D149, transformer oil, rate of increase = $500\ V\ s^{-1}$, 1.6–3.2 mm thickness	17.7	(10)
		Glass fiber and mineral filled	13.4–15.7	
Dielectric constant	–	40% glass fiber filled, 1 MHz, ASTM D150	3.8	(20)
		Glass fiber and mineral filled	4.6	
Dissipation factor	–	40% glass fiber filled, 1 MHz, ASTM D150	0.0013	(20)
		Glass fiber and mineral filled	0.016	
Volume resitivity	ohm cm	40% glass fiber filled, 2 min, ASTM D257	4.5×10^{16}	(20)
		Glass fiber and mineral filled	2.0×10^{16}	(20)
		Biaxially oriented PPS film	10^{17}	(6)
Arc resistance	s	40% glass fiber filled, ASTM D 495	35	(20)
		Glass fiber and mineral filled	200	
Comparative tracking index	V	40% glass fiber filled, UL 746 A	180	(20)
		Glass fiber and mineral filled	235	
Insulation resistance	ohm	40% glass fiber filled	10^{11}	(20)
		Glass fiber and mineral filled	10^{9}	
Thermal conductivity	$W\ m^{-1}\ K^{-1}$	At 20°C	0.29	(25)
Melt index (melt flow values)	$g\ (10\ min)^{-1}$	Uncured PPS (before curing steps)	3,000–8,000	(19)
		Powder coating PPS	1,000	
		PPS for mineral glass filled compounds	600	
		PPS for glass fiber filled compounds	60	
		Compression molding	0	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Maximum use temperature	K	UL temperature index for long-term use, for PPS resin	493	(26)
		PPS fiber for long-term use	505	(27)
			463	(28)
			>473	(29)
Decomposition temperature	K	Start of decomposition	698	(10)
		20% loss, thermogravimetric analyses of polymer, 10°C min^{-1}	823	
Water absorption	%	40% glass fiber reinforced PPS, 24 h immersion in water	0.03	(22)
		Glass and mineral filled PPS	0.03	
Oxygen index	–	Unfilled PPS, ASTM D2863	44	(10)
		40% glass fiber reinforced PPS	46.5	(10)
		Glass and mineral filled	53	(10)
		PPS fiber	34	(28)
			49	(29)
Flammability	–	Unfilled PPS, UL 94	V-0	(10)
		40% glass fiber reinforced PPS	V-0/5V	
		Glass and mineral filled	V-0/5V	
Flame spread index	mm	ASTM E 162	50.8	(20)
Autoignition temperature	K	–	813	(19)
Smoke density	min	Obscuration time, smoldering	15.5	(30)
		Obscuration time	3.2	
Important patents	U.S. Patent 3,354,129			(1)
	U.S. Patent 3,524,835			(31)
	U.S. Patent 3,717,620			(3)
	U.S. Patent 3,919,177			(4)
	U.S. Patent 4,645,826			(5)
Availability	kg	–	26,850,000	(32)
Suppliers	Phillips Petroleum, Borger,Texas, USA			
	Kureha Chemical, Tokyo, Japan			
	Toray, Tokyo, Japan			
	Hochest Celanese, Chatam, New Jersey, USA			

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Properties of special interest

Heat deflection temperature for glass fiber reinforced engineering plastics over 500 K: Poly(ether ether ketone) (PEEK), Nylon 6,6, poly(ethylene terephthalate), poly(butylene terephthalate)
UL temperature indices for long-term use over 450 K: Poly(ether ether ketone) (PEEK), poly(etherimide), poly(ether sulfone)
Flame resistance UL 94 V-O: Poly(ether ether ketone) (PEEK), poly(etherimide), poly(ether sulfone), polysulfone
Electrical conducting by the addition of dopants: Polyacetylene, poly(*p*-phenylene), polypyrrole[33]

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Poly(1,4-phenylene vinylene)

JACEK SWIATKIEWICZ AND PARAS N. PRASAD

ACRONYM, ALTERNATIVE NAME PPV, poly(*p*-phenylene vinylene)[1]

CLASS Polyaromatics

STRUCTURE $[-C_6H_4-CH{=}CH-]$

PROPERTIES OF SPECIAL INTEREST Electroactive and electroluminescent material. Electrical and electrooptical properties can be tuned by choice of doping and preparation procedure. Large third-order nonlinear optical susceptibility. Insoluble and infusible material, sustains high temperature treatment.

PREPARATIVE TECHNIQUES Thermal conversion of a soluble precursor polymer in oxygen free atmosphere.[2] Uniaxial stretch during thermal process yields highly anisotropic PPV films.[3]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	Flotation method Unit cell dimensions	1.24 1.283	(4)

Unit cell dimensions

Lattice	Monomers per unit cell	Cell dimensions (nm)			Cell angles			Setting angle* ϕ_s	Reference
		a	*b*	*c*	α	β	γ		
Monoclinic	2	0.790	0.605	0.658	123°	–	–	56–68°	(4)
Monoclinic	2	0.815	0.607	0.66	123°	–	–	–	(5)
Monoclinic	2	0.805	0.591	0.66	122°	–	–	56–68°	(6)
Monoclinic	2	0.80	0.60	0.66	123°	–	–	50° ± 2°	(7)

*Position of projected molecular major axis with respect to the *a*-axis direction.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Characteristic frequencies	meV (cm^{-1})	Inelastic incoherent neutron scattering (IINS)	2.5 (20) 7 (57) 15 (121) 25 (202) 37 (2990) 40 (3230) 51 (4120) 60 (4850) 68 (5500) 80 (6470)	(8)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
IR (characteristic absorption frequencies)	cm^{-1}	–	3,024	(9)
			1,594	
			1,519	
			1,423	
			965	
			837	
			784	
Raman (characteristic absorption frequencies)	cm^{-1}	–	1,628	(10)
			1,586	
			1,550	
			1,330	
			1,304	
			1,174	
			966	
Onset of the optical absorption band	eV	–	2.49	(11)
			2.4	(12)
			2.34	(13)
Wavelength at maximum of the band	nm	UV-Vis absorption	200	(11)
			244.8	(11)
			402	(11)
		80 K	511.9	(14)
Lowest even parity excited singlet state	eV	Two-photon fluorescence	2.95	(15)
		Two-photon absorption	3.58	(16)
Emission band	nm	Photo-luminescence	550	(17)
		80 K	522	(12)
		80 K	529	(14)
		77 K	531.5	(13)
		77 K	570.4	(13)
		77 K	615.3	(13)
		25 K	522	(18)
		25 K	562	(18)
		6 K	529	(19)
Tensile strength	MPa	Unoriented	41.2	(20)
		Oriented (draw ratio 6), in the machine direction	500	
		Oriented (draw ratio 5), transverse to the machine direction	31.7	
Young's modulus	MPa	Unstretched	3,200	–
		Oriented	37,000	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Elastic constants	MPa	Oriented (draw ratio 10) along 3 axis (draw direction)		(21)
		c_{11}	8,440	
		c_{13}	3,620	
		c_{33}	46,600	
		c_{44}	2,540	
Dielectric constant ε'	–	0.5 MHz	3.2	(22)
Index of refraction	–	3–25 μm, parallel*	2.1 ± 0.2	(9)
		3–25 μm, perpendicular* (oriented film)	1.5 ± 0.2	(9)
		1.064 μm, parallel	1.968	(23)
		1.064 μm, perpendicular (unoriented)	1.584	(23)
		0.633 μm, parallel	2.085	(23)
		0.633 μm, perpendicular	1.610	(23)
		0.633 μm, parallel	2.20	(24)
		0.602 μm, parallel	2.89(1)	(25)
		0.602 μm, perpendicular (oriented film)	1.63(1)	(25)
Nonlinear refraction coefficient (DFWM)	$cm^2\ W^{-1}$	0.800 μm, parallel (unoriented)	10^{-11}	(26)
Nonlinear absorption coefficient	$cm\ W^{-1}$	–	8.0×10^{-8}	–
		0.700 (probe), 0.620 (pump)	5.0×10^{-9}	(27)
		0.531 (probe), 1.064 (pump)	5.0×10^{-8}	(16)
$\chi^{(3)}$, DFWM	esu	0.580 μm	1.6×10^{-10}	(28)
		0.620 μm (unoriented)	1×10^{-10}	(28)
		0.602 μm, parallel	1.1×10^{-9}	(25)
		0.602 μm, perpendicular (oriented film)	5.8×10^{-11}	(25)
$\chi^{(3)}$, THG	esu	1.064/0.355 μm, parallel (oriented fim)	2×10^{-11}	(24)
		1.064/0.355 μm, parallel (unoriented film)	7.5×10^{-11}	(29)
Electronic conductivity	$S\ cm^{-1}$	$T = 298\,K$	10^{-11}	(30)
			2.2×10^{-14}	(31)
Electroluminescence emission peak	nm	ITO/PPV/AuAl/PPV/Au	562	(32)
			550	(33)
Quantum efficiency	%	ITO/PPV/Au	0.01	(32)
		Al/PPV/Au	0.01–0.1	(33)

* Light polarization orientation vs. polymer chain direction.

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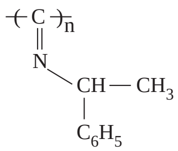
Poly(α-phenylethyl isocyanide)

CHANDIMA KUMUDINIE, JAGATH K. PREMACHANDRA, AND JAMES E. MARK

CLASS Poly(isocyanides); poly(iminoethylene); poly(isonitrile)

STRUCTURE



MAJOR APPLICATIONS Potential applications in mimicking biological macromolecules and applications in the areas of liquid crystals, coatings, column chromatographic supports, and polymer supported chiral catalysts.[1,2]

PROPERTIES OF SPECIAL INTEREST Chiral-helical rigid-rod structure and yields liquid crystals in solution.[1] Potentially useful as models for the understanding of the structure and properties of biological molecules.[3] Unreactive toward hydrogenation at ambient temperature and pressure and resistant toward acid hydrolysis.[4] One of the few soluble polyisocyanides of high molecular weight.[1]

OTHER POLYMERS SHOWING THIS SPECIAL PROPERTY Chiral helical structure: poly(*t*-butyl isocyanide) and poly(σ-tolyl isocyanide). Rigid-rod molecule: poly(*n*-hexyl isocyanate) and poly(*n*-butyl isocyanate).

Preparative techniques*

Conditions	Yield (%)	Reference
No initiator or solvent; temp.: 25°C	Small yield	(3, 5, 6)
Initiator: Ni(acetylacetonate)$_2$; solvent: ethanol; temp.: 25°C	80	(3)
Initiator: $NaHSO_4$, O_2, glass dibenzoyl peroxide; solvent: *n*-heptane; temp.: 50°C	60	(7)
Poly(l-α-phenylethyl isocyanide); initiator: H_2SO_4, O_2, glass dibenzoyl peroxide; solvent: *n*-heptane; temp.: 27°C	32	(7)
Poly(d-α-phenylethyl isocyanide); initiator: H_2SO_4, O_2, glass dibenzoyl peroxide; solvent: *n*-heptane; temp.: 27°C	23	(7)
Catalyst: $NiCl_2.6H_2O$, (R)-(+)-α-phenylethyl isocyanide	–	(8)
Concentrated H_2SO_4 at 40°C in air for 43 h	24	(9)
H_2SO_4 as a fine droplet dispersion in heptane, 25–100°C	–	(3)
H_2SO_4 acid, coated on powdered glass	–	(6, 9)
At room temperature, 0.1–5 mol% $NiCl_2 \cdot 6H_2O$, in methanol and with no solvent	60–95	(10, 11)

*For preparation of monomer see references (9, 10, and 12)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Typical comonomers	Sec-butyl isocyanide, methyl α-isocyanopropionate			(3)
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	131	–
Typical molecular weight range of polymer	$g\,mol^{-1}$	Osmometry	$M_n = (0.3–1.3) \times 10^5$	(3, 5)
			$M_n = (0.25–2.7) \times 10^5$	(12)
			$M_w = (0.5–2) \times 10^5$	(9)
		(RS)-poly(α-phenylethyl isocyanide), light scattering	$M_w = 3.4 \times 10^4$	(8)
		(R)-poly(α-phenylethyl isocyanide), light scattering	$M_w = 1.07 \times 10^5$	(8)
		–	Strongly depends on amount of catalyst	(10)
		Light scattering in toluene at 35°C	$M_w = 1.2$ and $1.5\ (\times 10^5)$	(6)
		Osmometry in toluene at 37°C	$M_n = 5.49$ and $7.55\ (\times 10^4)$	(6)
Degree of polymerization	–	(R)-poly(α-phenylethyl isocyanide), light scattering	817	(8)
		(RS)-poly(α-phenylethyl isocyanide), light scattering	260	
Typical polydispersity index	–	Fractionated samples	1.6–2.8	(3, 5)
		–	1.1–1.3	(3)
		Polymerization: ground-glass-sulfuric acid catalyst system	1.7–2.0	(6)
				(9)
		–	1.6–3.1	
IR (characteristic absorption frequencies)	cm^{-1}	N=C stretching	1,620–1,650	(10)
		Conjugated amine	1,625	(4)
		Nonconjugated amine	1,660	(4)
NMR	^{1}H NMR, in $CDCl_3$ and CCl_4			(13)
	^{13}C NMR, (R)-(+)-poly(α-phenylethyl isocyanide) at 23°C, in $CDCl_3$, 125.7 MHz			(8)
	d-Poly(α-phenylethyl isocyanide)			(3, 7)
	^{1}H NMR, in tetrachloroethylene, at 25°C and solid-state NMR			(7, 9)
Solvents	Soluble in more than 40 solvents			(3, 9)
	Soluble in apolar solvents (chloroform, benzene, petroleum ether)			(10)
	Copolymers with sec-butyl isocyanide is sparingly soluble in common solvents			(3)
	Copolymers with methyl α-isocyanopropionate have solubilities suitable for conventional solution charaterization methods			(3)
Nonsolvents	Insoluble in polar solvents (alcohols, water)			(10)

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Poly(α-phenylethyl isocyanide)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Second virial coefficient	mol cm^3 g^{-2}	In toluene, M_n = 20,000–123,000	Nearly invariant	(8)
		In toluene at 22°C, light scattering	0.2×10^{-4}	(14)
		In benzene at 22°C, light scattering	10^{-5} –10^{-6}	(14)
		–	2.86×10^{-4}	(15)
		–	5.87×10^{-4}	(15)
Solubility parameters	(MPa)$^{1/2}$	δ_d = due to dispersion forces, δ_p = due to permanent dipole-dipole forces, δ_h = due to hydrogen-bonding forces	$\delta_d = 19.68$, $\delta_p = 2.41$, $\delta_h = 5.15$	(9)
Cohesive energy density	(MPa)$^{1/2}$	–	9.56	(9)
Mark–Houwink parameters: K and a	K = ml g^{-1} a = None	Unfractionated poly(d, l-α-phenylethyl isocyanide), in toluene at 30°C	$K = 1.1 \times 10^{-2}$, $a = 0.8$	(3, 16)
		Fractionated poly(d, l-α-phenylethyl isocyanide), in toluene at 30°C	$K = 3.8 \times 10^{-5}$, $a = 1.30$	(3, 16, 17)
		In toluene at 30°C	$K = 1.9 \times 10^{-5}$, $a = 1.36$	(9)
		In tetrahydrofuran at 30°C	$K = 2.769 \times 10^{-5}$, $a = 1.35$	(16)
Huggins constant	–	For some fractions of $M_n > 38{,}000$ and for the unfractionated sample	0.59	(9)
		For some fractions of $M_n < 32{,}000$	1.24	
Radius of gyration	Å	X-ray scattering, in toluene	Not proportional to the mol. wt.	(3, 14)
		M_w = 13,000	28	(3)
		M_w = 45,800	55	(3)
		M_w = 91,500	80	(3)
Hydrodynamic radius	Å	(R)-poly(α-phenylethyl isocyanate), light scattering	51	(8)
		(RS)-poly(α-phenylethyl isocyanate), light scattering	23	
Monomer projection length	Å	Calculated using density = 1.12 g cm^{-3}	1.0	(1, 4)
		Using second virial coefficient of osmotic pressure data	1.02–1.04	(1)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Chain diameter	Å	X-ray scattering	15	(9)
			18	(3)
			15.1	(4)
Persistance length	Å	(R)-poly(α-phenylethyl isocyanide), in tetrahydrofuran, ~room temperature	32	(8)
		(RS)-poly(α-phenylethyl isocyanide), in toluene, ~room temperature, $M_w = 18{,}000$ g/mol, $R_g = 28$ Å	27	
		(RS)-poly(α-phenylethyl isocyanide), in toluene, ~room temperature, $M_w = 15{,}800$ g/mol, $R_g = 55$ Å	32	
		(RS)-poly(α-phenylethyl isocyanide), in toluene, ~room temperature, $M_w = 91{,}500$ g/mol, $R_g = 80$ Å	30	
		(RS)-poly(α-phenylethyl isocyanide), $M_w = 91{,}500$ g/mol, by Ni^{II} initiation	21	
Chain conformation	Nearly rigid rod like helix, by circular dichorism and optical rotatory studies			(3)
	Tightly wound helix with an overall shape of a cylindrical rod of about 15 Å diameter, 4_1 helix, by X-ray data			
Unit cell dimensions				(1, 3)
Lattice	–	–	Pseudo-hexagonal triclinic	
Cell dimensions	Å	–	$a = b = 14.92$, $c = 10.33$	
Cell angles	Degrees	–	$\alpha = 93.4$, $\beta = 90.5$, $\gamma = 118.2$	
Density	g cm^{-3}	–	1.12	(1)
Optical activity, molar specific rotation, $[M]_d$	deg cm^2 g^{-1}	d- and l-poly(α-phenylethyl isocyanide), at 27°C in toluene	~500	(1, 7, 9)
		In chloroform, poly(d-α-phenylethyl isocyanide)	−458	(10, 11)
Electrical conductivity	ohm m	At 1,000 psi pressure	10^{10}	(1)
Intrinsic viscosity	dl g^{-1}	$M_w = 107{,}000$, in chloroform at 25°C	0.57	(8)
		In toluene at 30°C	0.94	(9)
		In benzene at 25°C	0.760	(3)
		In toluene at 50°C	0.204	(3)
		In toluene at 27°C	1.94, 1.26	(3)

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Poly(α-phenylethyl isocyanide)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Decomposition temperature	K	Heating rate = 10° min^{-1}		
		In N_2 or Ar atmosphere	543	(9)
		In Ar atmosphere	513	(3)

Circular dichoric measurements[1]

λ (nm)	Film thickness (mm)	Solvent	Molar CD ellipticity (degree cm^2 dmol^{-1})
550–700	5.0	Methylenechloride	−560
480–500	5.0	Methylenechloride	+43,750
280–320	5.0	Methylenechloride	+257,320
550–700	3.0	Chloroform	−1,580
480–500	3.0	Chloroform	+23,830
280–320	3.0	Chloroform	+79,420
550–700	5.0	Dioxane	−13,230
480–500	5.0	Dioxane	−20,840
280–320	5.0	Dioxane	−1,620
550–700	10.0	Benzene	−39,000
480–500	10.0	Benzene	−50,180
280–320	10.0	Benzene	−14,280

Pyrolyzability[3]

	Conditions	Observation
Nature of product	IR spectroscopy	Pyrolysis at 500°C produces an intense broad infrared absorption band ~3,300 cm^{-1}, associated with N–H bonds Pyrolysates at 700°C reveal nitrile absorption at 2,270 cm^{-1} Nitrile absorption at 2,270 cm^{-1} becomes more intense in pyrolysates produced up to 1,300°C

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Poly(phenylmethylsiloxanes), cyclic

STEPHEN J. CLARSON

ACRONYM Cyclic PPMS

CLASS Cyclic polymers

STRUCTURE $-[(C_6H_5)(CH_3)SiO]_x-$

INTRODUCTION The molar cyclization constants from ring-chain equilibration reactions of poly(phenylmethylsiloxane) (PPMS) in both the bulk state and in solution were investigated in detail by Beevers and Semlyen.(1) Based upon these studies Clarson and Semlyen have described scaling up such reactions to successfully isolate cyclic poly(phenylmethylsiloxanes), that is, $-[(C_6H_5)(CH_3)SiO]_x-$, from ring-chain equilibration reactions carried out in toluene solution at 383 K.(2) Following fractionation, a variety of investigations of the physical properties of these cyclic polymers have be carried out and have also been compared with their linear polymer analogs. It should be noted that the large rings are atactic due to the equilibration used in their preparation. It is possible to obtain the stereoisomers of the small rings for this system, however. Although a rotational isomeric state model has been developed for the PPMS system by Mark and Ko,(3) no detailed calculations of the properties of the rings using this model have been described so far.

MAJOR APPLICATIONS Ring-opening polymerization of small rings to give linear PPMS high polymers. Copolymerization with other siloxane small rings to give copolymers of controlled composition.

PROPERTIES OF SPECIAL INTEREST Viscous fluids having good thermal stabilities. Certain stereoisomers when highly pure(1, 2, 4) are solids at room temperature.

PREPARATIVE TECHNIQUES Ring-chain equilibration reactions.(1, 2, 5, 6)

Selected properties of cyclic poly(phenylmethylsiloxanes) (r) compared to linear poly(phenylmethylsiloxanes) (l)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Characteristic ratio $\langle r^2 \rangle / nl^2$	–	Derived from molar cyclization equilibrium constants		(1, 5)
		Bulk state at 383 K	10.7	
		Toluene at 383 K	10.4	
		Derived from GPC; toluene at 292 K	8.8	(2, 6)
Critical dilution point	% Volume polymer	Toluene at 383 K	52	(1, 5)
Glass transition temperature $T_g(\infty)$	K	DSC	244.9	(6, 7)
Means square radius of gyration $\langle s^2 \rangle_{z,l} / \langle s^2 \rangle_{z.r}$	–	In benzene d_6 at 292 K	2.0	(6, 8)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dipole moment μ^2	Cm	$x = 5$	5.01×10^{-31}	(9)
Number-average molar masses of PDMS rings and chains	–	With the same GPC retention values M_r/M_l; toluene at 292 K	1.25 ± 0.05	(2, 6)
Enthalpy change	kJ mol^{-1}	For the formation of the *cis*-trimer	27	(1, 5)
		For the formation of the *trans*-trimer	22	
		For the formation of the *cis*-tetramer	8	

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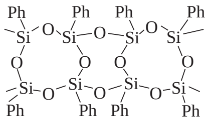
Poly(phenylsilsesquioxane)

RONALD H. BANEY

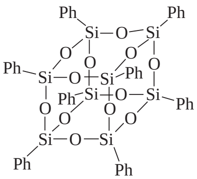
ACRONYMS, ALTERNATIVE NAMES, TRADE NAMES Phenyl-T, PPSQ, PPS, PLOS, CLPHS, phenyl silicobenzoic anhydryde, cyclolinear poly(phenylsiloxane), phenyl siliconic anhydride, Ladder Coat® (Mitsubishi Electric), Glass Resin® (Owens Illinois/ Showa Denko)

CLASS Polysiloxanes (siloxane ladder polymers)

STRUCTURES The structure of poly(phenylsilsesquioxane) probably depends upon the method of preparation. There is much debate still in the literature about its structure.[1] All of the structural types or combinations of the types shown may exist. The first table below summarizes the proposed structures and the evidence for such structures.

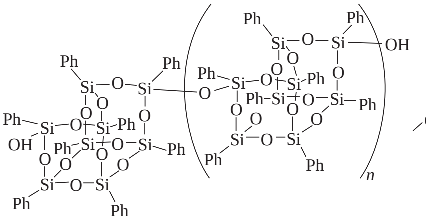


Ladder structure

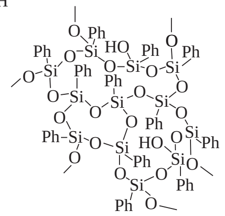


(T_8)

Cage structures



Partial cage structures



Random structure

MAJOR APPLICATIONS Interlayer dielectrics, high-temperature resins, and organic antireflective coatings.

PROPERTIES OF INTEREST Very high thermal stability (>500°C) and good dielectric properties.

RELATED POLYMERS Poly(alkylsilsesquioxane) and poly(*co*-silsesquioxanes): There are many references to these classes of materials,[1] but they are generally poorly characterized. Thus, they are not included in this handbook.

Structure, process, and molecular weight

PROPOSED STRUCTURE	PROCESS CONDITIONS	ACRONYM*	STRUCTURAL EVIDENCE	POLYMER $M_w \times 10^{-3}$ (g mol^{-1})	REFERENCE
Cage and oligomers	$PhSiCl_3$, H_2O, ether benzene and KOH	T-8	XRD	0.992	(2, 3)
Cis-syndiotactic double chain	Equilibration method $PhSiCl_3 + H_2O$ at 50% toluene to hydrolysate 0.1% KOH + 30% toluene at ~100°C to give "prepolymer" (I) or T-12 cage at ~250°C/ 90% solids in high boiling solvents	PPSQ-1	XRD, IR, UV Hypochroism, bond angle calculations, Mark–Houwink equation	4,100 —	(4, 5) (6)

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PROPOSED STRUCTURE	PROCESS CONDITIONS	ACRONYM*	STRUCTURAL EVIDENCE	POLYMER $M_w \times 10^{-3}$ ($g\,mol^{-1}$)	REFERENCE
Rigid chain polymers	Same as PPSQ-1 except final equilibration at 100% solids	PPSQ-2	High Kuhn segment Dynamo-optical (high negative segmental anisotropy)	– –	(7, 8) (9, 10)
Linked partial cages	–	PPSQ-1	Curvature in the Mark-Houwink equation Gelation at various temperatures, solvent types and concentrations	1,000	(11)
Cis-syndiotactic double chain	(1) $PhSiCl_3 + H_2O$ in MIBK $\sim 10^\circ C$ to hydrolysate (2) 0.1% KOH + 50 wt% solids in xylene reflux	PPSQ-3	IR	165	(12) (13)
Cis-syndiotactic double chain	Fluoride ion catalyzed equilibration of hydrolyzate	PPSQ-4	–	1,200	(14)
"Branched" ladder	$PhSiCl_3 + H_2O$ in ether or toluene to hydrolyzate to give "prepolymer" (I) with 30% dicyclohexyl-carboimide in xylene, 44% solids, 13 h, reflux	PPSQ-5a	FTIR, ^{1}H-NMR, ^{29}Si-NMR	12	(15, 16)
"Branched" ladder	(I) with 0.5% KOH in toluene, 44% solids, 13 h, reflux	PPSQ-5b	FTIR, ^{1}H-NMR, ^{29}Si-NMR	12	(15, 16)
Gel	(I) in toluene with 5% KOH, 44% solids, 13 h, reflux	PPSQ-5c	FTIR, ^{1}H-NMR, ^{29}Si-NMR	Gel	(15, 16)
Ladder	(I) in toluene and 8% diphenyl ether with 5% KOH, 40% solids, 13 h, 260°C	PPSQ-5d	FTIR, ^{1}H-NMR, ^{29}Si-NMR	26	(15, 16)
Ladder	(I) in 1:1 toluene and diphenyl ether, 0.005% KOH, 230°C, 5 h	PPSQ-5e	FTIR, ^{1}H-NMR, ^{29}Si-NMR	550	(15, 16)

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PROPOSED STRUCTURE	PROCESS CONDITIONS	ACRONYM*	STRUCTURAL EVIDENCE	POLYMER $M_w \times 10^{-3}$ ($g\,mol^{-1}$)	REFERENCE
Cis-isotactic double chain	(I) in 2:1:1:2 benzene-toluene-xylene-diphenyl ether with 10^{-4}% KOH, 7 h	PPSQ-5f	Eximer fluorescence	340	(17, 18)
"Ladder like"	$PhSi(OEt)_3$ in MIBK 20% solids with Et_4NOH, reflux, 12 h	PPSQ-6	Elemental analysis and molecular weight	5	(19)
Linked partial cages	Condensation of $(PhOHSiO)_4$	PPSQ-7	Insoluble amorphous gels	90	(20)
Cis-syndiotactic double chain	Condensation of $PhSi(OK)_3$	PPSQ-8	IR, XRD	72	(21)

*See reference (1).

Mark–Houwink parameter, *a*, for selected poly(phenylsilsesquioxanes)

PPSQ-	*a*	Molecular weight	Reference
1	0.92	1.4×10^4 (M_n)	(4)
2	1.10	2×10^5	(8)
2	0.90	0.6×10^3	(8)
2	0.9	$(2.5–3) \times 10^5$	(9, 10)
1	0.898	$(0.26–4.88) \times 10^5$ (M_n)	(22, 23)
2	0.70	3×10^5	(8)
1	0.54	2×10^5	(6)

Solution properties

PPSQ-	Soluble at room temperature	Insoluble at room temperature	Theta solvent	Reference
Oligomers	Benzene, chloroform, THF	Acetone , hexane, cyclohexane, ether, carbon tetrachloride, MIBK, isobutyl ether		(3)
1	Benzene, THF, methylene chloride	–		(4, 5)
2	Benzene, bromoform	–	Benzene/butylacetate (60:40)	(24)
5a,b,d,e,f	Benzene, toluene, THF	–	–	(15, 16)
8	Benzene, chloroform, ether, toluene, THF, methyl ethyl ketone, carbon tetrachloride, MIBK	Acetone, methanol, ethanol	–	(21)

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Mechanical properties

PPSQ-	Temp. (°C)	Tensile strength (MPa)	Elongation (%)	Reference
1	Room temp.	27.6–41.5	3–10	(25)
2	100	39	25	(10)
4	Room temp.	18–30	–	(14)
3	Room temp.	800	0.4	(13)
3	250	400	2.7	(13)
3	250	559	2.6	(1)

Persistence length

PPSQ-	Persistence length (Å)	Method	Reference
1	80	Yamakawa, Fujii method*	(27)
5f	64	Yamakawa, Fujii method*	(27)
2	100	diffusion in butyl acetate	(8)
2	89	$M[\eta]$ in bromoform	(8)
2	68	$M[\eta]$ in benzene	(8)

*See reference (26).

IR characteristic frequencies[15]

PPSQ-	Characteristic frequencies (cm^{-1})
1	1,130, Vs Si-Ar
	1,045, Vas Si-O-Si
1 with ''defects''	1,137

XRD

PPSQ-	*d* spacing (Å)	Reference
1	5.0, 12.5	(4)
1	4.6, 12.3	(10)

Thermal stability

PPSQ-	Thermolysis conditions	Temp. (°C)	Reference
1	Thermal balance in air-onset	525	(28)
3	TGA air, 10°C, min-onset	500	(29)
4	TGA air	505	(30)

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Other properties

PPSQ-	Specific dielectric constant	Thermal expansion coecient (ppm)	Pencil harness	Reference
3	–	(110–140) below 250°C	–	(13)
3	–	90 above 220°C	–	(13)
3	3.2 (1 kHz)	–	–	(31)
3	–	–	5H	(32)

Patented uses

Uses	Reference
Photoresists	(33–39)
Interlayer dielectric and protective coatings	(40–45)
Liquid crystal display elements	(46, 47)
Magnetic recording media	(48, 49)
Optical fiber coatings	(50, 51)
Gas separation membranes	(52)
Binders for ceramics	(53)
Carsinostatic drugs	(54)

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Poly(phenyl/tolylsiloxane)

DALE J. MEIER

ACRONYM PP/TS

CLASS Polysiloxanes

REPEAT TRIAD STRUCTURES –PPP–, –PPP′–, –PP′P′–, –P′P′P′–, –PPP″–, –PP″P″–, –P″P″P″–, –PPM′–, PPM″–, –PM″M″–, –M″M″M″–.
where P = $-Si(Ph)_2-O-$
P′ = –Si(Ph/*p*-T)–O–
P″ = $-Si(p\text{-}T)_2-O-$
M′ = –Si(Ph/*m*-T)–O–
M″ = $-Si(m\text{-}T)_2-O-$
Ph = phenyl
p-T = *p*-tolyl
m-T = *m*-tolyl.

MAJOR APPLICATIONS The various PP/TS polymers are not commercial.

PROPERTIES OF SPECIAL INTEREST Highly crystalline, high melting point, excellent thermal stability, mesomophic state at high temperatures.

PREPARATIVE TECHNIQUES	CONDITIONS	REFERENCE
Anionic	Initiators for cyclic trimers	
	Li alkyl, solution	(1, 6, 7)
	$KO-[Si(Ph/Tol)-O]_n-K$, solution, bulk	(2–5)

PROPERTY	UNITS	POLYMER	CONDITIONS	VALUE	REFERENCE
Solvents	K	–PPP– –P″P″P″–	Diphenyl ether c1-Chloronaphalene 1,2,4-Trichlorobenzene	>420	(1–3, 8)
		–PPP –P″P″P″–	Quenched from solution	315	(7)
		–PPP′– –PP′P′– –PPP″– –P″P″– –PPM″– –PM″M″– –M″M″M″–	Toluene Chloroform	300	(1–4)

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PROPERTY	UNITS	POLYMER	CONDITIONS	VALUE	REFERENCE
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None		Chloroform, 40°C	$K \times 10^{-3}$ / a	(10)
		−PPP′−		2.1 / 0.83	
		−PPP″−		2.6 / 0.83	
		−P′P′P′−		2.4 / 0.83	
NMR chemical shifts	ppm	−PPP′−	^{29}Si	−46.16, −45.83	(1)
		−PPP″−	^{29}Si	−45.66, −56.99	(1)
		−P′P′P′−	^{29}Si	−46.49	(1)
		−M″M″M″−	^{13}C	20.87 (CH_3)	(5)
Tensile strength	MPa	−PPP′−	Films from toluene or chloroform	<0.2	(4)
		−PPP″−		<0.2	
		−PPM′−		<0.2	
		−PPM″−		<0.2	
		−PM″M″−		2.5	
		−M″M″M″−		3.5	
Elongation at break	%	−PM″M″−	Films from toluene or chloroform	130	(4)
		−M″M″M″−		13	

Crystalline state properties[3]

Polymer	Lattice	Cell dimensions (nm) *a*	*b*	*c*	Monomer per cell
−PPP′−	Rhombic	2.106	1.053	1.036	2
−P′P′P′−	Rhombic	2.104	1.086	0.997	2

−PPP′−:

d-spacings (nm) Layer line number	Electron diffraction	X-ray diffraction
0	1.053	1.052
	0.940	0.940
	0.526	–
	0.476	0.467
	0.421	0.429
	0.391	0.393
2	0.492	0.498
	0.464	0.467
	0.450	0.448
	0.425	–
	0.367	0.363
3	0.326	–
	0.324	0.325
4	0.259	–

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d-spacings (nm)	Layer line number	Electron diffraction	X-ray diffraction
	0	1.052	1.053
		0.960	0.960
		0.520	–
		–	0.526
		0.455	0.468
	1	–	0.757
		–	0.468
	2	0.483	–
		0.455	–
		0.445	0.443
		0.420	0.423
	3	0.335	–
		0.317	–
		0.249	–

PROPERTY	UNITS	POLYMER	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	–PPP′–	From experimental	1.12	(3)
		–P′P′P′–	From unit cell	1.17	
			From experimental	1.13	
			From unit cell	1.24	
Melting temperature	K	–PPP–	To mesomorphic state	538, 545	(1, 8)
			To isotropic state	813	(1)
		–PPP′–	To mesomorphic state	458	(1)
			To isotropic state	733	(1)
		–PPP″–	To mesomorphic state	413	(1)
			To isotropic state	703	(1)
		–P′P′P′–	To mesomorphic state	433	(1)
			To isotropic state	723	(1)
		–P″P″P″–	To mesomorphic state	573	(1)
			To isotropic state	>753 (decomp.)	(1)
		–M″M″M″–	To mesomorphic state	404	(6)
			To isotropic state	803	(6)
Glass transition temperature	K	–PPP–	From DSC	313, 322	(1, 9)
		–PPP′–		313	(1)
		–PPP″–		313	(1)
		–P′P′P′–		323	(1)
		–P″P″P″–		323	(1)
		–M″M″M″–		268	(6)
Thermal stability	K	–PPP′–	TGA, 10% weight loss, $10^{\circ}\ min^{-1}$ under N_2	756	(1)
		–PPP″–		727	(1)
		–P′P′P′–		742	(1)
		–P″P″P″–		789	(1)
		–M″M″M″–		731	(6)

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Polyphosphates

BRUCE M. FOXMAN

CLASS Inorganic and semi-inorganic polymers

STRUCTURE $-[O-P(O_2)]_n-O-$ or $-[P(O)(OR')-O-R-O]_n-$

MAJOR APPLICATIONS *Acids:* Intermediate in fertilizer production. Catalysts for alkylation, dehydrogenation, polymerization, and isomerization. Dehydrating agent in dye and pigment production. *Salts:* Builders in detergent and cleaning formulations. Consistency control agents in foods. Deflocculants in clays, dyes, and ink. Anticalculus agents in toothpaste and mouthwash. Dispersants for solids in clay processing, drilling mud, and pigments. Flame retardation. Models for natural biopolymers.(1–3)

PREPARATIVE TECHNIQUES Principal synthetic routes: condensation and addition reactions. A useful survey is available.(1)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Theta temperatures Θ	K	Lithium polyphosphate in LiCl (0.4 M)/H_2O	293.2	(4)*
		Lithium polyphosphate in LiBr (1.80 M)/H_2O	298.2	(5)
		Sodium polyphosphate in NaBr (0.415 M)/H_2O	298.2	(6)
Glass transition temperature	K	Hydrogen polyphosphate	263	(7, 8†)
		Lithium polyphosphate	608	
		Sodium polyphosphate	553	
		Calcium polyphosphate	793	
		Strontium polyphosphate	758	
		Barium polyphosphate	743	
		Zinc polyphosphate	793	
		Cadmium polyphosphate	723	
Characteristic ratio $\langle r^2\rangle_o/nl^2$	–	Sodium polyphosphate (aqueous NaBr, 0.35–0.415 M) 25°C	6.6	(6)
		Cesium polyphosphate (aqueous CsCl, 0.96 M) 30°C	7.1	(9, 10)

*Strauss and Anders (1962) suggested that the results obtained for the theta temperature of lithium polyphosphate in 0.4 M LiCl should be ''regarded with caution.''

†In Eisenberg and Sasada (1965), glass transition temperatures were measured by using an automatic device which measured the length of the polymer sample as a function of temperature.

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Percentage composition of the strong phosphoric acids*[(11)]

P_2O_5 (wt. %)	$\frac{[P_2O_5]}{[H_2O]}$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	HIGH-POLY
67.4	0.263	100.0														
68.7	0.279	99.7	0.33													
70.4	0.302	96.2	3.85													
71.7	0.321	91.0	8.86													
73.5	0.352	77.1	22.1	0.79												
73.9	0.360	73.6	25.1	1.34												
75.7	0.394	53.9	40.7	4.86	0.46											
77.5	0.438	33.5	50.6	11.5	2.68	0.74										
79.1	0.481	22.1	46.3	20.3	7.82	2.26	1.02	0.34								
80.5	0.523	13.8	38.2	21.0	13.0	6.86	3.38	1.67	1.03	0.22						
81.0	0.542	12.2	34.0	22.7	14.6	8.42	4.36	2.27	1.41	0.56						
81.2	0.549	10.9	32.9	22.3	15.0	9.36	5.41	2.85	1.75	0.97	0.36	0.05				
82.4	0.594	7.32	23.0	19.3	15.9	12.3	8.21	5.73	3.89	2.52	1.36	0.91	0.14			
84.0	0.667	3.92	11.8	12.7	12.0	10.5	8.97	7.99	6.62	5.63	4.54	3.72	3.03	2.46	1.68	6.63
85.0	0.717	2.28	6.36	7.32	8.01	8.17	7.67	7.22	6.93	6.42	5.89	5.27	4.69	3.99	3.83	16.9
85.3	0.736	1.87	4.73	6.33	6.58	6.66	6.71	6.36	6.11	5.88	5.46	5.07	4.90	4.64	4.38	25.6
86.1	0.787	1.46	2.81	3.74	4.43	4.52	4.77	4.79	4.93	4.67	4.54	4.67	4.63	4.38	4.17	43.5
87.1	0.860	0.83	1.81	2.17	2.53	3.09	3.39	3.46	3.33	3.55	3.47	3.45	3.52	3.26	3.24	61.1
87.9	0.920	0.50	0.82	1.56	1.76	1.72	2.03	2.13	2.26	2.07	2.26	2.06	2.20	1.99	2.30	76.4
89.4	1.066	1.88	1.52	0.77	0.61	0.62	0.68	0.54	0.71	0.86	1.03	0.98	1.16	1.23	1.37	86.8

*For total % $P_2O_5 \geq 86.1$, small amounts of trimeta- and tetrametaphosphoric acid were also detected. 1 = ortho-, 2 = pyro-, 3 = tri-, 4 = tetra-phosphate, etc. Highpoly = higher-molecular-weight material including 15-phosphoric acid.
(Source: Jameson 1959. Reprinted with permission from the Royal Society of Chemistry.)

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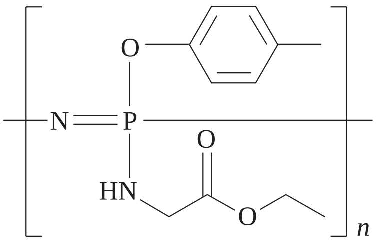
Poly(phosphazene), bioerodible*

JOSEPH H. MAGILL

ACRONYM PPHOS

CLASS Polyphosphazene

STRUCTURES Poly[(*p*-methylphenoxy)-co-(ethylglycinto)phosphazene] (50/50: mole ratio)



MAJOR APPLICATIONS Polymers have shown promise as bioerodible materials capable of (controlled degradation and sustained drug delivery for therapeutic and other related uses.[1–14] Polyphosphazenes have been evaluated for approximately two decades, but research has become more focused in recent years.

PROPERTIES OF SPECIAL INTEREST In general, tailored side groups (see the section on polyphosphazene synthesis below) enable a wide variety of hydrolytic properties to be designed into selected polymers for applicatons in biological environments for sustained drug administration without the release of harmful degradation products at physiological concentrations.[1,3,6–9] Limited modeling studies have been conducted.[14]

SYNTHESIS TECHNIQUES AND TYPES OF POLYMERS Polymer with specific poly(phosphazene) structures that are susceptible to hydrolytic degradation under physiological conditions. Examples with glucosyl, amino acid ester, imidazolyl, glycerol side groups have been synthesized.[9] Besides this, side groups have also been grafted (through direct γ irradiation) onto PBFP polymers particularly for bicompatibility enhancement.[11,12]

In vitro evaluations have been made. Bioerodible poly(phosphazenes) have the advantage that the degradation products are biocompatible. The majority of bioerodible poly(phosphazenes) have been synthesized by the classical thermal procedure of Allcock et al. (1965)—reference (15). The copolymer in question is described.[1,3] In vivo performances in clinically relevant conditions are planned for PPHOS matrices.

*There is a paucity of tabulated release data on bioerodible polymers. Thus, the author has presented some results interpolated from graphical plots of controlled release for matrices at different Inulin, that is, $(C_6H_{10}O_5)_x$ loadings.[1] Different drug loadings and release rates were monitored in vitro and modulated through changes in pH. Surface inspections of the matrices were conducted by using surface-scanning electron microscopy techniques to characterize changes in texture.[1]

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Chemical structure and properties

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular mass (of repeat units)	$g\,mol^{-1}$	For the basic unit illustrated above	254.2	—
Typical molecular weight	$g\,mol^{-1}$	Variable for the same reasons; $M_w \sim 1 \times 10^6$ by GPC		—
Typical polydispersity M_w/M_n	—	Variable but usually broad for kinetic evaluations made to date on account of synthesis procedures that were employed		(2)

Release rates for 50/50 polyphosphazene copolymer(1)

CONDITIONS	TIME (days)	VALUE (% mass loss day^{-1})	TIME (days)	VALUE (%mass loss day^{-1})
Inulin loadings at 40% in copolymer at pH = 2.0; S.D. ± 3; error < 10%	0.0	0.0	5.1	96.4
	0.07	9.0	7.1	98.8
	0.1	25.4	9.0	98.9
	0.3	49.0	12.0	99.5
	1.0	68.6	15.0	99.6
	3.0	85.5	25.0	100.0
	4.0	89.4		
Ditto (at 10% loading)	0.0	0.0	7.2	37.8
	0.1	0.6	10.2	43.5
	0.5	4.8	13.1	47.3
	1.1	10.4	17.1	51.4
	2.2	18.3	21.1	54.5
	4.0	27.0	24.0	57.4
Ditto (at 1% loading)	0.2	0.84	10.2	29.3
	0.5	8.2	14.1	34.3
	1.1	11.9	18.0	38.8
	3.1	17.7	22.0	40.7
	6.2	23.9	24.0	42.3
Inulin loadings at 40% in copolymer at pH = 7.4; S.D. ± 3; error < 10%	0.0	0.01	9.1	77.8
	0.1	0.5	12.0	78.6
	0.2	25.5	15.0	79.4
	0.5	42.1	18.0	79.9
	2.1	62.7	22.0	79.7
	4.2	70.5	24.0	79.5
	6.2	77.3		

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CONDITIONS	TIME (days)	VALUE (% mass loss day^{-1})	TIME (days)	VALUE (%mass loss day^{-1})
Ditto (at 10% loading)	0.0	0.0	9.0	26.7
	0.2	4.4	12.0	28.7
	0.5	10.1	14.0	30.0
	1.0	14.4	17.0	32.0
	2.0	18.3	20.0	33.6
	4.2	21.5	24.0	35.0
	6.2	24.8		
Ditto (at 1% loading)	0.0	0.0	10.1	22.5
	0.6	7.9	13.1	23.9
	1.0	9.6	16.0	25.4
	2.1	13.0	20.1	27.9
	4.2	16.0	22.1	28.7
	6.2	18.5	24.0	30.0
	8.1	20.7		
Inulin loadings at 40% in copolymer at pH = 10; S.D. $\pm$ 3; error $<$ 10%	0.0	0.0	7.1	88.1
	0.1	13.5	9.1	88.4
	0.4	43.0	13.1	88.7
	1.1	60.6	17.1	88.8
	3.0	77.8	24.1	89.2
	5.0	83.6		
Ditto (at 10% loading)	0.0	0.0	7.0	36.4
	0.5	8.9	10.1	38.4
	2.1	21.3	13.0	40.5
	2.1	29.3	16.0	42.5
	4.1	34.0	23.0	43.3
Ditto (at 1% loading)	0.0	0.0	11.0	33.6
	0.5	13.7	14.0	34.8
	2.2	18.0	17.1	35.7
	5.1	24.5	22.0	36.2
	8.1	29.4	24.0	36.2

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Poly(phosphazene) elastomer

JOSEPH H. MAGILL

ACRONYM, TRADE NAME PNF elastomer, EYPEL-F

CLASS Polyphosphazenes

STRUCTURE $-[-N{=}P-(OCH_2CF_3)(OCH_2(CF_2)CH_yF_x)-]_n-$
($y = 0$, F = 3, or $y = 1$, F = 2)

MAJOR APPLICATIONS Developmental quantities of PNF and EYPEL-F and other elastomers were manufactured in quantity for high-performance seals, collapsible storage tanks, O-rings, and vibration shock absorption mounts in military and other devices. The service life of these items is claimed to be relatively long and reliable.

PROPERTIES OF SPECIAL INTEREST High-cost items for commercialization, but this is less critical where they have potential applications as biomaterials such as soft denture liners, blood-compatible parts (prostheses), drug-related release agents and the like. Other more mundane uses encompass fire-resistant paint additives, agrichemicals, and herbicides, proofing of textiles of diverse kinds, lubricants, and fire-resistant fluids (as low molecular weight and cyclic compounds), and many more possibilities.

SYNTHETIC TECHNIQUES AND TYPES OF SYNTHESIS (a) Thermal two-stage polymerization (ring-opening of hexachlorocyclotriphosphazene followed by nucleophilic substitution).[1] (b) Mixed nucleophiles have also produced useful elastomers[2–8] using the same two-step procedure. (c) Now better defined block and random polymers with elastomeric properties have been developed and characterized.[9,10]

PROPERTY	VALUE	REFERENCE
Molecular mass of repeat unit	Variable, depending upon the side groups copolymer type and composition	–
Typical molecular weight	Variable, depending upon the side groups, copolymer type, and composition	–
Typical polydispersity index M_w/M_n	Variable (usually high and broad in thermal synthesis)	–
Solvents	Methyl isobutyl ketone, methyl ethyl ketone, acetone, dimethylformamide, tetrahydrofuran, 1-methyl-2-pyrrolidine, acetonitrile and related polar solvents	(6, 8, 11)
	Freon and freon ether type solvents are best for the more heavily fluorinated polymers	(8)
Nonsolvents	Hydrocarbons (aliphatic and aromatic) petroleum products, hydraulic fluids, water-glycol, aqueous ammonia, acetic acid, and the like	(6)

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Mechanical properties

PROPERTY	UNITS	CONDITIONS*	VALUE		REFERENCE
Tensile modulus (100%)	MPa	–	1.4–10.5		(4, 6)
			Below T_g	Above T_g	
Dynamic modulus	–	PNF elastomer, radiation	(193 K)	(353 K)	(12)
Storage modulus	MPa	vulcanized, unfilled; 110 Hz	1,590	0.401	
Loss modulus	MPa		1,580	0.396	
Dynamic modulus	–	PNF elastomer, peroxide	–	0.0515	(12)
Storage modulus	MPa	vulcanized, (30 pph of FEP	2,520	4.56	
Loss modulus	–	carbon black)	2,520	62.2	
			4.48	86.8	
Dynamic modulus	MPa	PNF elastomer, peroxide	2,080	3.46	(12)
Storage modulus	–	vulcanized (30 pph Silanox	2,080	3.40	
Loss modulus	–	101 silica)	–	0.620	
Yield strain L/L_o	%	–	100–350		(4, 6)
Hardness	Shore D	–	40–90		(4, 6)
Tear strength	$kN\,m^{-1}$	–	7.0–17.5		(4)
Compression set	%	70 h at 423 K, in air	20–50		(4)
Flexible modulus	MPa	At 273 K	17.2		(4)
		At 233 K	44.8		
		At 200 K	222		
Flexural Gehman freeze point	K	ASTM D-1053	205		(4)

*Aging changes in mechanical behavior of PNF elastomers were reported with time, temperature, degree of cross-linking (radiation and chemical), and fluid and other environmental conditions for in-service evaluations ASTM and other practical tests were employed. Property changes and conditions are detailed in several references.[4,5,11]

Rheological measurements are expressed graphically as loss moduli G'' and storage moduli G' versus shear rate respectively.[4,6] Dynamic torsional braid analysis (TBA) spectra over a wide range of temperatures and several frequencies depicted significant transitional behavior in the region of T_g, T,[1] and beyond.[13]

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Solution properties

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Theta temperature Θ	K	Methyl isobutyl ketone	298		(8)
Interaction parameter χ	–	MIBK, 298 K	0.49		(8)
Second virial coefficient	mol cm^3 g^{-2}	DMF at 298 K; $M_w = 23–126\ (\times 10^5)$; $M_n = 3.2–6.7\ (\times 10^5)$	2.8–11.0 $[A_2 = (1.1 \times 10^{-3}) M_w^{-0.35}]$		(8)
Mark-Houwink parameters: K and a	K = ml g^{-1} a = None	–	$K = 2.62 \times 10^{-3}$ $a = 0.52$		(8)
Huggins constants: k' and k''	–	MIBK; 298 K	$k' \times 10^2$	$k'' \times 10^2$	(8)
		THF	1.09	−2.08	
		MEK	1.47	−4.06	
		Acetone	0.89	−0.91	
		Acetonitrile	0.77	−0.98	
		DMF	0.46	−0.16	
			0.87	−0.28	
Characteristic ratio $\langle r^2 \rangle_0 / nl^2$	–	MIKB; 298 K	25–35		(8)
Persistence length	Å	MIKB; 298 K	42–64		(8)
Radius of gyration $\langle S^2 \rangle_z^{1/2}$	Å	DMF; 298 K; $M_w = 23–126\ (\times 10^5)$; $M_n = 3.2–6.7\ (\times 10^5)$	340–890		(3, 8)
		Solvent E2* (9.09% acetone) at 295 K; $M_n = 15.5 \times 10^4$; MW $= 6.8 \times 10^6$	870		(3)
		Solvent E2 at 295 K; MW $= 42.8 \times 10^4$; MW $= 10.0 \times 10^6$	930		(3)

*Solvent E2 is F−$(CFCF_3CF_2O)_2CHFCF_3$, manufactured by DuPont Freon Products Division, Wilmington, Deleware, USA.

Anomalous changes are frequently noted for fractions across the broad molecular weight distribution(s). For example, $k' + k'' \neq 0.5$—see references (3) and (4). Intrinsic viscosity parameters as a function of percent acetone in E2 solvent are plotted in figure 3 of reference (3) for several PNF fractions. Many other values are tabulated by Hagnauer and Schneider in this reference along with many other solution parameters. Recently, the solution properties of polyphosphazenes have been critically reviewed.[14] Besides polymer quality, there have been problems with ''tailing'' in the fractionation of fluorinated polyphosphazenes as pointed out in reference (15). The quality polymers synthesized since the 1990s[9, 10, 16] should circumvent these problems that have been encountered with dilute solution and other kinds of characterization.

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Stabilities: Flammability properties

PROPERTY	UNITS	CONDITIONS	VALUE			REFERENCE
Oxygen index:* LOI =	%	PNF sheet , mole %: Percent trifluoroethoxy/ fluoroalkoxy (65/35)	UF (Radiation vulcanized)	30 phr C (peroxide vulcanized)	30 phr silica (Peroxide vulcanized)	
$100[O_2]/[O_2] + [N_2]$	%		48	65	47	(17)
			48	–	–	(18)
Burn velocity†	$mm\,s^{-1}$	In 75% oxygen	1.65	0.05	0.7	(17)
Smoke density	Relative	Optical cell	~1	~2.5	~0.7	(17)
Average residue	Relative	At 773 K				(17)
		Air	4	26	26	
		N_2	6.5	28.5	29	
Residue	K	Temperature for 10% loss				(17)
		At $10\,K\,min^{-1}$				
		Air	650	669	693	
		N_2	659	659	690	
		For 50% loss				
		Air	701	717	735	
		N_2	710	712	735	
Activation energy (degradation)	$kcal\,mol^{-1}$	Air	30.5	35.4	23.3	(17)
		Nitrogen	31.5	33.9	14.5	
Glass transition temperature	K	DSC	484	482	483	(17)

*Test = ASTM D2863.
†During burning, dripping may distort the result. These values fall sharply with increasing incident radiation (heat flux) on the specimen.

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Poly(phosphazene), semicrystalline

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ACRONYMS, ALTERNATIVE NAME PBFP, PTFP, PBTFP, PFPN, PF, poly[(2,2,2,-trifluoroethoxy)phosphazene]

CLASS Polyphosphazenes

STRUCTURE $-[N{=}P(OCH_2CF_3)_2]_x-$

MAJOR APPLICATIONS Produced for many years in developmental quantities for evaluation in research and limited use in commercial tests and military applications; nonflammable fibers and films. Under evaluation for controlled drug delivery systems, hydrogels, implants, and membranes.

PROPERTIES OF SPECIAL INTEREST Low-temperature flexibility and high-temperature stability, high oxygen index and low flame spread rate, hydrophobic (low surface tension), good carbon solvent resistance, biocompatibility, mesophase formation, and polymorphism.

SYNTHESIS TECHNIQUES (a) Stokes[1] thermally polymerized hexachlorocyclotriphosphazene via a ring-opening process to provide a cross-linked elastomer, but it was not until 1965 that a high molecular poly(dichlorophosphazene) was isolated and subsequently transformed, via nucleophilic substitution, into thermally stable semicrystalline homopolymers.[2–4] This procedure was used widely to synthesize a variety until a few years ago, but it suffered from relatively low conversions (<70% so as to avoid cross-linking), unknown chain-end groups and lack of molecular weight control of the product. These difficulties obstructed its commercialization.

(b) Other thermally induced polymerization techniques have been developed employing Lewis acid catalysed solution polymerization[5–7] of the hexachlorocyclic monomer as well as by polycondensation of $Cl_3P{=}N{-}P(O)Cl_2$[8] and the thermal polymerization of phosphoranimines[9,10] to provide many alkyl and aryl substituted phosphazenes, but this procedure also has processing disadvantages.

(c) Still, well-defined poly(phosphazenes) with high conversions, known end-groups, and molecular weight control were first prepared less than ten years ago by employing the anionically initiated polymerization of phosphoranimines to produce well-defined homo, block, and random copolymers.[11–14]

(d) Recently, a living cationic polymerization of phosphoranimines with molecular weight control has been developed to produce polyphosphazenes of of similar quality to (c).[15–17]

Now that polymerization control has been established, these techniques may lead to cost-effective and new developments/applications in this interesting class of polymers. Some physical properties that are sensitive to structure and chain conformations may require further investigation. Some of these polyphosphazenes are to be found among the polymers that follow.

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PROPERTY	UNITS	CONDITIONS	VALUE
Molecular mass of repeat unit	$g\,mol^{-1}$	–	243.04
Typical molecular weight	$g\,mol^{-1}$	Daltons	$< 2 \times 10^3$ to 3×10^7
Typical polydispersity index (M_w/M_n)*	–	–	~1.2–20

*Low polydispersity polyphosphazenes (P.I. between 1 and 2) are novel and were first synthesized less than a decade ago.

Morphology[18]

PROPERTY	UNITS	CONDITIONS	VALUE
Birefringence (spherulites and mesophase moieties)*	–	Relative values measured on stepwise (a) heating/(b) cooling of thin solution-crystallized negative spherulites:	
		(a) Heating; orthorhombic (folded chains)	
		293 K	1.064
		318 K	1.121
		325 K	1.179
		328 K	1.250
		333 K	1.267
		338 K	1.297
		Mesophase (2-dimensional chain, extended)	
		393 K	3.298
		413 K	3.078
		433 K	3.500
		(b) Cooling; (2-dimensional chain, extended)	
		413 K	3.540
		402 K	3.345
		393 K	3.148
		373 K	3.308
		353 K	3.314
		(b) Orthorhombic (3-dimensional chain, extended)	
		332 K	2.783
		322 K	2.640
		313 K	2.756
		293 K	2.540

*The pattern observed here is analogous to that encountered in dilatometry measurements (see phase transitions in the tables on *Transition temperatures* below). The birefringence is always negative in sign but increases in magnitude as the morphology changes from the solution cast chain-folded to the columnar chain-extended pseudohexagonal form (see the table on *Crystalline-state properties* below). The birefringence stabilizes upon cycling (heating/cooling) and subsequently follows a set pattern after a few cycles. Hereafter, the pathway is reversible between orthorhombic to/from the mesophase during heating and cooling. Crystallization directly from the melt produces smectic and batonnet morphologies of high crystallinity, not classical spherulites (of 35–50% crystallinity) that only grow from moderately concentrated polymer solutions.

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Properties of unique block and random methoxyethoxy (MEO)/(trifluoroethoxy) (TFO) phosphazene copolymers*[19]

Random	m	$M_w \times 10^{-3}$	M_w/M_n	T_g (K)[a]	$T_{(1)}$ (K)[b]	$\Delta H_{T_{(1)}}$ ($J\,g^{-1}$)[c]	T_m (K)[d]	Density ($g\,cm^{-3}$)[e]
Mole fraction	0.000	99.0	1.46	–	356	47.0	495	–
"m" of MEO	0.028	94.7	1.78	215	344	40.5	480	1.690
	0.053	77.0	1,92	212	335	36.0	464	1.612
Block								
Mole fraction	0.126	65.8	1.60	–	315	21.9	446	1.431
"m" of MEO	0.047	173.7	1.36	220	353	46.2	493	1.690
	0.080	178.2	1.56	211	341	38.8	478	1.664
	0.126	77.1	1.57	–	339	27.0	455	1.591
	0.134	62.2	1.34	211	321	21.7	421	1.583

*Side group placement and composition of methoxyethoxy produces a wide variety of properties that range from crystalline low "m" (<0.126) with morphologies akin to the PBFP homopolymer, to higher "m" (>0.134) where these crystalline transformations cease to exist. All polymer exhibit thermotropic behavior. Anionically initiated polymerization of $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSi(CH_3)_3$ followed by the addition of $(CF_3CH_2O)_3P{=}NSi(CH_3)_3$, except for random copolymers where each of two polymerizations were conducted concomitantly.

[a] T_g = glass transition temperature.
[b] $T_{(1)}$ = mesophase transition temperature.
[c] $\Delta H_{T_{(1)}}$ = enthalpy of $T_{(1)}$ transition.
[d] T_m = melting temperature; values were determined optically.
[e] At 25°C via flotation in CsCl solution.

Spectroscopic properties

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
UV (characteristic absorption frequencies)	μm	Electronic spectra absorption	220; 400 weak 270–280 diffuse	(20, 21)
IR (characteristic frequencies)	cm^{-1}	FT-IR	1,420; 965; 880	(22, 23)
		P–O–C		
		P–N	1,280	
		P–O–P	870–1,000	
		Stretching and bending vibrations (for cross-linking) –P=N– stretching	1,250–1,330	
FT-IR (Nicolet 5DXB)	cm^{-1}	Solid (well-defined) PBFP polymer by KBr		(24)
		Aliphatic CH	2,981	
		CH	1,462	
		P–O–C	1,427	
		P=N (br)	1,271–1,308	
		P=O	1,173; 963	
		C–O	1,089	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
NMR (Solution) (Brüker AM 500) 202 MHz for ^{31}P and 125 MHz for ^{13}C measurements	ppm	^{31}P Dipolar-^{1}H Decoupled ^{13}C ^{19}F (3 atoms) ^{1}H dipolar-coupled ^{13}C (reference peak) TMSi (reference 0 ppm)	7.5 −6.9 120.7–127.3 64.3 −6.9	(25)

PROPERTY	CONDITIONS	VALUE	REFERENCE
NMR (solid state); ^{1}H dipolar decoupled; ^{13}C (MAS at 2–4 kHz); no decoupling for ^{31}P spectra; reference H_3PO_4 (0 ppm); Brüker MSL 300; analysis made at 121.5 MHz for ^{31}P and 75.5 MHz for ^{13}C	Solution crystallized sample: $M_w = 300,000$; $M_w/M_n = 2.3$; $T_m = 515$ K, $T_g = 207$ K; heating/cooling spectra recorded/10 K stepwise from 293–373 K (i.e., through $T_{(1)}$ mesomorphic transition)	Two peaks (mobile/immobile) in the ^{31}P spectra below $T_{(1)}$ and one mobile narrower peak about this transition, where side groups and chains are all mobile; above $T_{(1)}$ the phase is 2-D pseudohexagonal; below $T_{(1)}$ a 3-D highly crystalline form exists	(26)
NMR (wide line)	^{1}H, ^{13}C, and ^{19}F nuclei studied under stepwise heating/cooling; $T_{(1)} = 353$ K; $T_m = 513$ K; intrinsic viscosity = 1.06 dl g^{-1} in THF, 298 K	Rotating backbone in a hexagonal lattice above $T_{(1)}$ and enhanced side group motions; single narrow line ~0.4 Oe for ^{19}F; ~0.6 Oe for ^{1}H; ^{31}P narrows to 1.1 Oe as compared to 2.4 Oe at 20°C indicating rigidity	(27)
Spin-lattice ^{1}H NMR relaxation times	Semicrystalline sample; $M_w = 2 \times 10^5$; $M_w/M_n = 1.75$; $T_{(1)}$ of cast film from THF = 348 K; measurement range = 303–443 K	The ^{13}C measurements made through $T_{(1)}$ for CH_2 and CF_3 side groups are 1.75 and 3.55 respectively with activation energies of ~17.3 and 13.7 kJ mol^{-1} obtained from ln τ versus T (K^{-1})	(25)
NMR (solid echo), 90 MHz	Semicrystalline sample; $M_w/M_n = 1.75$; film cast from THF at 348 K; range of measurement = 303–443 K	Molecular motions above and below $T_{(1)}$ fitted with Weibull functions using τ_2 relaxation values below and above the $T_{(1)}$ transition	(28)

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Equations of state

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Thermal expansion coefficient	K^{-1} ($\times 10^{4}$)	X-ray		(29–31)
		(i) Solution cast film	1.74	
		(ii) Melt cast film	2.7	
		a-axis expansion (linear)	1.8	
		Dilatometry: semicrystalline crystalline orthorhombic phase (volume)	$\alpha_c = 2.48$	(31)
		Mesophase ($T_{(1)}$ to T_m)	$\alpha_t = 6.99$	(32)
		(volume)	$\alpha_t = 6.24$	(32)
		Isotropic ($\geq T_m$)	$\alpha_l = 9.25$	(31)
		(volume)	$\alpha_l = 8.67$	(32)
		Monoclinic (initially below $T_{(1)}$) (volume)	$\alpha_m = 6.83$	(25)
Volume change in transition regions	ΔV%	Dilatometry		(25, 31)
		$T_{(1)}$ transition (orthorhombic to mesophase)	~6	
		T_m transition (mesophase to isotropic)	~5–6	
		$T_{(1)}$ transition (monoclinic to mesophase)	~3	
Thermo-mechanical analysis (TMA)	ΔV%	$T_{(1)}$ transition	~5	(31–33)
		T_m transition	~6	
Thermal (volume) expansion coefficient	K^{-1} ($\times 10^{-4}$)	Solution cast α-form,* (monoclinic) below $T_{(1)}$	7.5	(25)
Density*	$g\,cm^{-3}$	α-form		(25)
		303 K	1.665	
		311 K	1.655	
		321 K	1.643	
		331 K	1.632	
		334 K	1.629	
		338 K	1.621	

*Densities are also presented graphically for the δ-hexagonal (columnar) phase and the chain-extended γ-orthorhombic form of high crystallinity and the isotropic phase above T_m under conditions of heating and cooling. See the corresponding birefringence and transitional data under corresponding temperatures in the table on *Morphology* above.

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Poly(phosphazene), semicrystalline

Pressure properties

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Compressibility coefficient β	bar^{-1} ($\times 10^{-4}$)	From P–V–T data* Pressure (MPa)	$<T_{(1)}$ (at 298 K)	$>T_{(1)}$ (at 498 K)	(34)
		0.1	0.46	1.12	
		50	0.42	0.95	
		100	0.37	0.71	
		200	0.33	0.59	
		300	0.25	0.37	
		400	0.21	0.28	
		650	0.19	0.22	
Thermal expansion coefficient α	K^{-1} ($\times 10^{-4}$)	Graphs for pressures = 0.1–700 MPa; 298–460 K (approximate)	$<T_{(1)} = 2.4$ At $T_{(1)} = 7.0$ $>T_{(1)} = 9.2$		(34)
Gruneisen parameter	–	At 303 and 220 K	4.6		(34)
Density	$g\,cm^{-3}$	As a function of pressure and temperature	Data represented graphically		(34)
Compression modulus K_v	bar or (GPa)	Pressure dependence of compression modulus	Plotted as function of pressure up to 600 MPa through $T_{(1)}$ transitions		(34)

*$M_w \sim 1 \times 10^6$; $M_w/M_n \sim 1.2$; solid, mesophase, and liquid states at various pressures and temperatures (interpolated).

Solution properties*

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Theta Θ temperature	K	Tetrahydrofuran	298	(20)
Interaction parameter χ_1	–	In graphical form	Estimates	(36)
Second virial coefficient	$mol\,cm^3\,g^{-2}$	THF, 298 K, $M_w = 1.48 \times 10^6$	1.0×10^{-3}	(23)
		Acetone, 298 K, $M_w = 1.54 \times 10^6$	5.1×10^{-4}	(23)
		Cyclohexanone, 298 K, $M_w = 1.42 \times 10^6$	6.7×10^{-5}	(23)
		Cyclohexanone, 298 K, $M_w = 2.92 \times 10^{-5}$, $M_n = 1.3 \times 10^5$	4.7×10^{-5}	(37)
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None	THF (details not given since coefficients change across the MW distribution)	$K = 620$ $a = 0.85$	(37)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Huggins constant k_H	—	THF, 298 K, $M_w = 1.48 \times 10^6$ Acetone, 298 K, $M_w = 1.54 \times 10^6$ Cyclohexanone, 298 K, $M_w = 1.42 \times 10^6$	$\sim$0.02 0.30 0.42	(23)
Intrinsic viscosity $[\eta]$	—	Fractions in methyl isobutyl ketone (MIBK)	(4.89×10^{-3})	(37)

*Anomalous behavior is noted among some of the solution properties since polymers are not always well-defined.

Crystalline-state properties* (29, 30, 38)

Comments†	Lattice	Monomers per unit cell	Unit cell dimensions a	b	c	Cell angles α	β	γ	Crystal density ($g\,cm^{-3}$)
Form α	Orthorhombic	2	10.14	9.35	4.86	—	—	—	1.748
Form β	Monoclinic	2	10.03	9.37	4.86	—	91°	—	1.767
Form γ	Orthorhombic	4	20.60	9.40	4.86	—	—	—	1.715
Form δ	Hexagonal	(?)	d(100)γ	10.3(200°C)		—	—	—	1.354 (estimate)

*Crystalline modifications (semicrystalline polymorphic states and mesophase). See the expansion coefficient as a function of temperature in the table on *Equations of state* above.
†Form α = chain-folded from THF solution; Form β = low molecular weight from pseudohexagonal (columnar) mesophase; Form γ = melt quench from isotropic melt 250°C to room temperature as chain-extended orthorhombic form; Form δ = low molecular weight from pseudohexagonal (columnar) mesophase.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Crystallization kinetics	—	Isothermal growth rate and form depend upon undercooling measured by DSC and polarized light transmission method (also known as the DLI technique)	See reference for details	(39)
Avrami exponent	—	Transformations kinetics for: (1) Isotropic to (2-D) mesophase; that is, sub-T_m (K) (2) 2-D mesophase to orthorhombic (3-D); that is, sub-$T_{(1)}$ (K)	 2 2	(39)

Transition temperatures*

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature T_g	K	Differential scanning calorimetry Dynamical mechanical Torsional braid analysis	207 — 220	(3, 25, 33, 36, 40–42) (43) (44)
Mesophase phase transition $T_{(1)}$	K	Dilatometry DSC and TMA DSC	338–365 365 339–363	(24, 30, 47) (33, 36, 40) (44–46)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Mesophase phase transition $T_{(1)}$	K	Dielectric analysis	(See graphed data in appropriate section below)	
		Torsional braid analysis	~331	(44)
		Creep compliance	338–343	(30)
		DLI (transmitted light)	–	(39, 46)
$T_{(1)}$ relationship equilibrium $T^0_{(1)}$	K	Best fit to data (estimated)	$T_{(1)} = 371 - (1{,}288)M_w^{-0.37}$ $T^0_{(1)} = 371$	(41)
Melting (isotropization) transition (T_m)	K	DSC	515 513–515 519, 522	(All of the above and more)
Melting temperature ($T_m \equiv T_i$)	K	"Fit" to relevant experimental data	$T_m = 539 - 1{,}904\ M_w^{-0.39}$	(41)
Equilibrium melting temperature	K	–	$T^0_m = 539$	(44)
T_g, $T_{(1)}$, and T_m interrelationship	K	"Fitted" to oxy-type polymers from a linear plot of $(T_m - T_g)/(T_m - T_{(1)})$ vs. $T_{(1)}/T_m$	$3.2(T_m)^2 - [T_g + 8.2T_{(1)}]T_m + 6[T_{(1)}]^2 = 0$	(25, 40)
		For all data including trifluoroethoxy/alkoxy copolymers	$2.4(T_m)^2 - [T_g + 6.2T_{(1)}]T_m + 4.7[T_{(1)}]^2 = 0$	(41)

*All transition temperatures depend on factors such as sample MW and conditions of measurement. Note that α- , β-, and mesophase transition values depend upon the measurement method, molecular weight, and specimen history. Consult references for the techniques employed. For example, some authors claim (with good reason) that dynamical techniques are only related to classical dilatometry (1^0 min^{-1}) results. Logically, all comparisons should be on similar time scales.

Mechanical properties

PROPERTY	UNITS	CONDITIONS	VALUE			REFERENCE
Tensile modulus	MPa	$M_\eta = 2.97 \times 10^6$; $M_w/M_n < 1.4$	Unlisted			(48)
Tensile strength	MPa	Solution cast film	196			(48)
Elongation at break	%	Solution cast film	700			(48)
Some typical values in the transition regions†			$<T_g$ (165 K)	$<T_{(1)}$ (312 K)	$>T_{(1)}$ (380 K)	(43)
Dynamic modulus (E)*	MPa	Unoriented cast film; $d = 1.695\ g\ cm^{-3}$; $M_w > 10^6$; 110 Hz	1,170	130	11.8	
Storage modulus E'	MPa	Unoriented cast film; $d = 1.695\ g\ cm^{-3}$; $M_w > 10^6$; 110 Hz	1,170	130	11.8	

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PROPERTY	UNITS	CONDITIONS	VALUE			REFERENCE
Some typical values in the transition regions[†]			$<T_g$ (165 K)	$<T_{(1)}$ (312 K)	$>T_{(1)}$ (380 K)	(43)
Loss modulus E''	MPa	Unoriented cast film; $d = 1.695\ g\ cm^{-3}$; $M_w > 10^6$; 110 Hz	29.0	19.1	0.89	
Dynamic modulus E^*	MPa	Same film oriented × 9; $d = 1.692$; 110 Hz	8,670	455	76.8	
Storage modulus E'	MPa	Same film oriented × 9; $d = 1.692$; 110 Hz	8,670	455	57.7	
Loss modulus E''	MPa	Same film oriented × 9; $d = 1.692$; 110 Hz	971	12.9	9.28	

[†] Thermo-mechanical spectra have been measured from 153 to 413 K at 3.5 and 110 Hz respectively; only selected values are presented here.

Electrooptical and magnetic properties

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Index of refraction n	—	PBFP in ethyl acetate solution; $M_w = 18 \times 10^6$; $[\eta]_{THF} = 410$	1.37	(49)
Refractive index increment dn/dc	$g\ mol^{-1}$	PBFP in ethyl acetate solution; $M_w = 18 \times 10^6$; $[\eta]_{THF} = 410$	0.004	(49)
Dielectric constant ε'	—	ε' plots from 100 Hz to 100 kHz in the range 78–393 K	See graphs	(50, 51)
Dielectric loss ε''	—	ε'' plots from 100 Hz to 100 kHz in the range ~78–393 K	See graphs	—
Dielectric strength	$V\ mil^{-1}$	—	360	(52)
Dipole moment of monomer unit μ_{110}	Debye	—	9.0	(49)
Optical anisotropy (segmental) $(\alpha_1 - \alpha_2)$	cm^3	*Cis-trans* conformation (assumed)	160×10^{-2}	(49)
Kerr constant	$cm^5\ g^{-1}\ (300\ V)^{-1}$	Electric birefringence in EtOAc solution	7.0	(49)
Shear optical coefficient $[n]/[\eta]$	$cm^3\ g^{-1}$	Dynamic birefringence in solution	12	(49)
Relaxation time τ	s	—	2–9 ($\times 10^{-4}$)	(49)

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Surface and interfacial properties

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Surface tension	$mN\,m^{-1}$	Contact angle (microscopy)	16	(53)
		Zisman plots	16.5	(53)
		Contact angle (degradation after prolonged UV irradiation)	16.5–14.4	(54)
Interfacial free energy	$erg^2\,cm^{-4}$	From isothermal crystallization studies	30	(39)
	$erg\,cm^{-2}$	At (2-D to 3-D) interface	~10 (estimate)	

Optical properties

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Refractive index increment dn/dc	$ml\,g^{-1}$	Tetrahydrofuran at 298 K	0.023		(55)
			0.0233		(41)
			0.0232		(23)
		Cyclohexanone at 298 K	0.053		(23)
		Acetone at 298 K	0.019*		(23)
		Freon* E-2/acetone: 10/1 (v/v)	0.048		(56)
Refractive index n	–	Tetrahydrofuran at 298 K	1.405		(23)
		Acetone at 298 K	1.360		
		Cyclohexanone at 313 K	1.448		
Intrinsic viscosity $[\eta]$	$(dl\,g^{-1})$	Acetone with TBAN† at 298 K TBAN (mol)	$[\eta]$	k'	(23)
		0.0	3.70	0.03	
		0.01	2.02	0.29	
		0.02	2.04	0.19	
		0.05	2.07	0.18	
Radius of gyration	Å	$MW = 3.0 \times 10^6$	~660		–
Power factor	–	Frequency $= 10^2$–10^6 Hz	10^{-3} to 40×10^{-3}		(42, 52)

*Freon E2 is $-(CFCF_2O)_2-CHFCF_2$, from DuPont Freon Products Division, Wilmington, Deleware, USA.
†Tetrabutyl ammonium nitrate used as an ''aggregate breaker.'' Other salts have been employed to prevent ''tailing'' in GPC analysis.[(55)]

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Degradation stabilities

PROPERTY	CONDITIONS	VALUE	REFERENCE
Thermal degradation:* poly(tri-fluoroethoxy-phosphazene) (homopolymers)	Polymer made by ring-opening thermal synthesis: polymerization (MW uncontrolled, chain-ends unknown)	Depolymerization to cyclics, followed by chain scission at weak points (i.e., defects in the backbone) followed by rapid depolymerization to cyclic oligomers	(57)
		Random chain scission followed by partial unzipping of fragments to cyclic oligomers	(58)
		Depolymerization by chain scission and subsequently partial unzipping with some chain end initiation; reaction order of 0.8 proposed	(59)
		Initiation occurs at chain ends with subsequent depolymerization and chain transfer; some chain scission occurs at weak points in the backbone	(60)
		Two stage initiation, followed by backbone rearrangement and subsequently chain scission at resultant weak links within the backbone	(61)
Homo- and copolymers†	Polymer made by anionically initiated polymerization with MW, chain-end and chain-sequence control with defect-free chains	Depolymerization with chain end initiation followed by complete unzipping to cyclic trimer by a cationic mechanism; stability of the copolymers decreases by incorporating and increasing alkoxyalkoxy side group	(62)

*Phosphazene polymers with halogenated side chains give rise to toxic gaseous products, based upon ''overall hazard rating,'' ALH, involving thermal stability, flammability, and toxicity parameters (RD_{50} and LC_{50}). Halogen-free polyphosphazenes are preferred over halogen-containing polymers for high-temperature applications. For example, see reference (64) for graphical details and analysis.

†The results represent the first thermal degradation study that has been conducted on well-defined polyphosphazenes. They also provide an unambiguous answer to the actual mechanism of degradation in these polymers.

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Transport properties

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Permeability P*: (sorption and time-lag techniques)	cm^3(STP)cm cm^{-1} s^{-1} Pa^{-1} ($\times 10^{12}$)	Semicrystalline film: $T_g = 198$ K; $T_m = 491$ K; $T_{(1)} = 343$ K; $\alpha = 6.24 \times 10^{-4}$ K^{-1}.		(63)
		Permeant gas (298 K)		
		He	7.10	
		Ne	3.15	
		Ar	2.05	
		Kr	1.93	
		Xe	1.75	
		H_2	4.74	
		O_2	2.66	
		N_2	1.10	
		CO_2	1.47	
		N_2O	1.62	
		CH_4	1.43	
		C_2H_6	1.47	
		C_2H_4	2.69	
		C_3H_8	1.25	
		Permeant gas (300 K)		
		O_2	1.50	
		N_2	1.21	
	cm^3(STP)cm cm^{-1} s^{-1} Pa^{-1} ($\times 10^{11}$)	Mesophase, above $T_{(1)}$; $\alpha = 8.67 \times 10^{-4}$ (K).		(32)
		Permeant gas (348 K)		
		He	3.93	
		Ne	2.09	
		Ar	1.97	
		Kr	2.04	
		Xe	2.11	
		H_2	3.48	
		O_2	2.26	
		N_2	1.25	
		CO_2	8.78	
		CH_4	1.64	
		C_2H_6	1.68	
		C_2H_4	2.68	
		C_3H_8	1.44	

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Permeability coefficient P	$cm^3\ cm\ cm^{-3}\ s^{-1}\ cm^{-1}\ Pa^{-1}$ ($\times 10^6$)	Semicrystalline solution cast film; $M_n \sim 3 \times 10^7$; $M_w/M_n < 1.4$.			(48)
		Permeant gas	Activation energy (kJ mo1^{-1})		
		$He^{\dagger}$	15.8	17.2	
		$Xe^{\dagger}$	24.8	3.45	
		$O_2{}^{\dagger}$	21.5	5.40	
		$N_2{}^{\dagger}$	24.3	2.33	
		$CO_2{}^{\dagger}$	13.1	27.7	
		$CH_4{}^{\dagger}$	25.4	2.7	
		$He^{\ddagger}$	15.7	68.6	
		$Xe^{\ddagger}$	15.2	31.6	
		$O_2{}^{\ddagger}$	16.3	37.5	
		$N_2{}^{\ddagger}$	19.3	21.3	
		$CO_2{}^{\ddagger}$	11.2	108.6	
		$CH_4{}^{\ddagger}$	16.3	28.1	
Diffusivity coefficient D: (sorption and time-lag techniques)	$cm^2\ s^{-1}$ ($\times 10^7$)	Semicrystalline film; $d = 1.707\ g\ cm^{-3}$; $T_g = 198\ K$; $T_m = 491\ K$; $T_{(1)} = 343\ K$; $\alpha = 6.24 \times 10^{-4}$ (K).			(63)
		Diffusant gas (298 K)			
		He		343.0	
		Ne		438.5	
		Ar		21.61	
		Kr		10.52	
		Xe		4.46	
		H_2		161.8	
		O_2		27.83	
		N_2		17.15	
		CO_2		12.66	
		N_2O		13.42	
		CH_4		11.30	
		C_2H_6		3.61	
		C_2H_4		5.91	
		C_3H_8		1.29	
		Mesophase above $T_{(1)}$ transition; $\alpha = 8.67 \times 10^{-4}$ (K).			(32)
		Diffusant gas (348 K)			
		He		771.0	
		Ne		338.0	
		Ar		130.0	
		Kr		54.6	
		Xe		50.8	
		H_2		540.0	
		O_2		154.0	
		N_2		122.0	
		CO_2		97.3	
		CH_4		97.9	
		C_2H_6		47.4	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Diffusivity coefficient D: (sorption and time-lag techniques)	$cm^2\ s^{-1}$ ($\times 10^7$)	Mesophase above $T_{(1)}$ transition; $\alpha = 8.67 \times 10^{-4}$ (K).		
		Diffusant gas (348 K)		
		C_2H_4	66.5	
		C_3H_8	25.1	
Solubility coefficient S	cm^3(STP) cm^{-3} Pa^{-1} ($\times 10^7$)	Semicrystalline film; $d = 1.707\ g\ cm^{-3}$; $T_g = 198$ K; $T_m = 491$ K; $T_{(1)} = 343$ K; $\alpha = 6.24 \times 10^{-4}$ (K).		(63)
		Solubilant gas (298 K)		
		He	2.07	
		Ne	2.72	
		Ar	9.47	
		Kr	18.36	
		Xe	39.2	
		H_2	2.93	
		O_2	9.55	
		N_2	6.44	
		CO_2	11.63	
		N_2	12.07	
		CH_4	12.62	
		C_2H_5	40.85	
		C_2H_4	45.4	
		C_3H_8	97.0	
		Mesophase above $T_{(1)}$ transition.		(32)
		Solubilant gas (348 K)		
		He	5.10	
		Ne	6.20	
		Ar	15.15	
		Kr	37.35	
		Xe	41.4	
		H_2	6.44	
		O_2	14.7	
		N_2	10.2	
		CO_2	90.0	
		CH_4	16.65	
		C_2H_6	35.40	
		C_2H_4	40.20	
		C_3H_8	57	

*Measurements have also been reported—reference (48)—for some of these same gaseous permeants in the range 293–403 K for an HMW polymer ($\sim 10^7$ Daltons).

†Permeant gas, above $T_{(1)}$, $K > 350$.

‡Permeant gas, below $T_{(1)}$, $K < 350$.

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Poly(phosphonates)

BRUCE M. FOXMAN

CLASS Inorganic and semi-inorganic polymers

STRUCTURE $-[P(O)(R')-O-R-O]_n-$

MAJOR APPLICATIONS Flame retardation. Corrosion-resistant and improved adhesion coatings. Prevention of gingivitis and dental caries. Adjuvants and thickeners in textile dyeing. Scale inhibitors. Molding resins.[1,2]

PREPARATIVE TECHNIQUES Principal synthetic routes: condensation and addition reactions. A useful survey is available.[1]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperatures	K	R = 4,4′-biphenol; R′ = phenyl	393	(3)*
		R = 3-(4-hydroxyphenyl)-1,1,3-trimethyl-5-indanol; R′ = phenyl	401	(3)
		R = 9,9-bis(4-hydroxyphenyl)fluorene; R′ = phenyl	438	(3)
		R = 4,4′-sulfonyldiphenyl; R′ = phenyl	419	(4)†
		R = 4,4′-thiodiphenyl; R′ = phenyl	362	(4)
Decomposition temperatures	K	R = 4,4′-biphenol; R′ = phenyl	668	(3)
		R = 3-(4-hydroxyphenyl)-1,1,3-trimethyl-5-indanol; R′ = phenyl	633	(3)
		R = 9,9-bis(4-hydroxyphenyl)fluorene; R′ = phenyl	683	(3)
		R = 4,4′-sulfonyldiphenyl; R′ = phenyl	738	(4)
		R = 4,4′-thiodiphenyl; R′ = phenyl	738	(4)

*In Imai et al. (1983), glass transition temperatures were determined from DTA and TMA curves. Also, decomposition temperatures were determined as the temperature at which 10% weight loss occurred, as determined by TGA.

†In Kim (1983), glass transition temperatures were determined by using DSC results; the midpoint in the baseline shift was taken as the glass transition temperature. Also, decomposition temperatures are quoted as the temperature at which 10% weight loss occurred, as determined by TGA.

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Polypropylene, atactic

CHARLES L. MYERS

ACRONYM, TRADE NAMES a-PP, AFAX®, REXTAC®, EASTOFLEX®

CLASS Poly(α-olefins)

STRUCTURE $-[CH_2CHCH_3]-$

MAJOR APPLICATIONS Low molecular weight atactic polypropylene is used as a component of hot melt adhesives and sealants.[1] ''Atactic'' polypropylene which is produced as a by-product of isotactic PP production is not ideally atactic or completely amorphous.[2,3] Ideally atactic polypropylene has been prepared by hydrogenation of poly(2-methyl-1,3-pentadiene), that is, poly(1,3-dimethyl-1-butenylene) or PDMB.[4] Recently, directly synthesized atactic polypropylene and other amorphous poly(α-olephins) (APAO or APO) have been developed.[1,2,3,5,6] Lower molecular weight versions are commercial products.[1,6,7] High molecular weight versions are being evaluated as elastomers and as blend components for modification of isotactic polypropylene.[2,3,5,6]

PROPERTIES OF SPECIAL INTEREST Tensile strength, extensibility, recovery, softening temperature, hardness, melt viscosity, and compatibility with other polyolefins and adhesive formula components.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	(a) Nonmetallocene a-PP		(2)
		(b, c) Metallocene a-PP		
		(a) $M_w = 29{,}000$, $M_w/M_n = 6$	0.8626	
		(b) $M_w = 200{,}000$, $M_w/M_n = 3.3$	0.8606	
		(c) $M_w = 490{,}000$, $M_w/M_n = 2.3$	0.8550	
		Hydrogenated PDMB, $M_w = 23{,}300$, $M_w/M_n = 1.03$	0.8542	(8)
		Temperature dependence, 80–120°C, $x = (-0.19 \times 10^{-4})t - (3.05 \times 10^{-6})t^2$	$0.848 - x$	(9, 10)
Thermal expansion coefficient	K^{-1}	80–120°C	$(6.1–9.3)\times10^{-4}$	(9, 10)
Crystallinity	%	DSC, XRD		(2)
		(a) $M_w = 29{,}000$, $M_w/M_n = 6$	Some	
		(c) $M_w = 490{,}000$, $M_w/M_n = 2.3$	None detected	
Refractive index increment dn/dc	$ml\,g^{-1}$	Hydrogenated PMBD, cyclohexane		
		30°C	0.0989	(4)
		20°C	0.0844	(8)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Head-to-head content	%	NMR (metallocene a-PP) (Bernoullian statistics)	None detected	(3)
		NMR (hydrogenated PDMB) (Bernoullian statistics)	None detected	(4)
Glass transition temperature	K	DSC, hydrogenated PDMB		
		$M_w = 23{,}300$	268	(8)
		$M_w = 40{,}800$	266.9	(4)
		$M_w = 33{,}400$	270.6	(4)
		Hercules AFAX™ 600 HL-5	255	(4)
		Fractionated a-PP	265.5	(4)
		Average a-PP	260	(4, 11)
		Commercial APAO homopolymer, DSC		
		Rexene Rextac™ 2115	252	(1)
		Eastoflex™ P1010 and P1023	263	(7)
Radius of gyration, $R_G/M^{1/2}$	Å $mol^{0.5}g^{-0.5}$	Hydrogenated PDMB, 298 K, SANS	0.336	(8)
		Several a-PP citations, Theta, IV	0.333	
Chain dimension temperature coefficient $d\ln\langle R^2\rangle_0/dT$	K^{-1}	Hydrogenated PDMB, melt, SANS	-0.1×10^3	(8)
		Theta, IV several a-PP citations	$(-1.0$ to $-3.0) \times 10^{-3}$	
Characteristic ratio, $6R_G^2/N_w nl^2$	–	Hydrogenated PDMB, 298 K, SANS	6.1	(8)
		Several a-PP citations, 298 K, Theta, IV	6.2	(8)
		311 K	5.8–5.9	(4)
Mark–Houwink parameters: K and a	K = ml g^{-1} a = None	Decalin 135°C	$K = 1.066 \times 10^{-4}$ $a = 0.804$	(8)
Theta temperature	K	2-Octanol, hydrogenated PDMB	310.6	(4, 12)
		1-Octanol	350	(12, 13)
		Biphenyl	402	(12, 14)
Entanglement molecular weight	g mol^{-1}	413 K, measured	4,600	(15)
		413 K, calculated	5,400	
		298 K, measured	3,500	
		298 K, calculated	4,100	
Tensile strength	MPa	Compression molded, ASTM D412		(2)
		(a) $M_w = 29{,}000$, $M_w/M_n = 6$	1	
		(b) $M_w = 200{,}000$, $M_w/M_n = 3.3$	1	
		(c) $M_w = 490{,}000$, $M_w/M_n = 2.3$	2	
		APAO, Eastoflex™ P1010 and P1023	1.38	(7)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Maximum extensibility	%	Compression molded, ASTM D412		(2)
		(a) $M_w = 29{,}000$, $M_w/M_n = 6$	110	
		(b) $M_w = 200{,}000$, $M_w/M_n = 3.3$	1,400	
		(c) $M_w = 490{,}000$, $M_w/M_n = 2.3$	2,000	
		APAO, Eastoflex™ P1010	200	(7)
		APAO, Eastoflex™ P1023	100	(7)
Tensile set	%	300% elongation, 20 cm min^{-1}, 10 min hold under stress, 10 min relax		(2)
		(a) $M_w = 29{,}000$, $M_w/M_n = 6$	Break	
		(c) $M_w = 490{,}000$, $M_w/M_n = 2.3$	76	
		(a) 100% elongation	45	
		(c) 100% elongation	14	
Flexural modulus	MPa	Compression molded, ASTM D5023		(2)
		(a) $M_w = 29{,}000$, $M_w/M_n = 6$	10	
		(b) $M_w = 200{,}000$, $M_w/M_n = 3.3$	8	
		(c) $M_w = 490{,}000$, $M_w/M_n = 2.3$	5	
Hardness	°Shore	Shore A, compression molded		(2)
		(a) $M_w = 29{,}000$, $M_w/M_n = 6$	67	
		(b) $M_w = 200{,}000$, $M_w/M_n = 3.3$	50	
		(c) $M_w = 490{,}000$, $M_w/M_n = 2.3$	55	
Hardness	dmm	Penetration, ASTM D-5, APAO		
		Homopolymers: Rextac™ 2115	5	(1)
		Eastoflex™ P1010 and P1023	20	(7)
Softening point	K	Ring and ball, ASTM E-28, APAO		
		Homopolymers: Rextac™ 2115	426	(1)
		Eastoflex ™ P1010 and P1023	423, 428	(7)
Melt viscosity	Pa s	Brookfield, 190°C, ASTM D-3236, APAO		
		Homopolymers: Rextac™ 2115	1.425	(1)
		Eastoflex™ P1010 and P1023	1.0, 2.3	(7)

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Polypropylene, elastomeric (stereoblock)

CHARLES L. MYERS

ACRONYMS, TRADE NAMES ELPP, elPP, REXFLEX®, SUPERSOFTPP®

CLASS Poly(α-olefins)

STRUCTURE $-[CH_2CHCH_3]-$

MAJOR APPLICATIONS The polymers referred to in this chapter include those families of homopolymers of propylene which are known to have elastomeric recovery properties at reasonable molecular weight and for which properties have been attributed to a crystallizable-noncrystallizable (e.g., isotactic-atactic) stereoblock structure, or to a major component with a stereoblock structure, whether or not the compositions are homogeneous by solvent fractionation tests. Copolymers and blends are not deliberately included in the data presented, but are described in some of the references. (See also some of the closely related elastomeric polymers presented in the entry on *Polypropylene, atactic* in this handbook.) The criterion of multiple crystallizable blocks per polymer chain may be met in significant fractions of low-tacticity, low-stereoregularity polymers of very high molecular weight.

Elastomeric polypropylenes are being actively studied in academic and industrial laboratories. Some materials are in the pilot developmental stage. Some flexible polyolefins, with moderate elastomeric recovery, are currently being evaluated on a larger scale.[1] Potential applications include fiber, film, and extruded goods.

PROPERTIES OF SPECIAL INTEREST Strength, modulus/flexibility, recovery, degree of thermal resistance, and solubility/extractability. Mechanical properties in the following table are intended to represent best published examples of the respective types.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	Buoyancy method, calculated from data in reference (2) for 19–31% crystallinity	0.8683–0.8787	(2)
		–	<0.9	(3)
		–	0.88–0.89	(1)
Glass transition temperature	K	DSC	262.9–261.5	(2)
			265	(4)
Melting temperature	K	DSC peak endotherms (broad temperature range)		(5)
		16% mmmm	325, 352	
		28% mmmm, peak range	398–418	
		DSC several examples, broad range, peak endotherm	417–418	(2)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melting temperature	K	DSC, 45–54% mmmm, dual endotherm peaks ranges	323–327, 352–346	(6)
		DSC, broad range, dual endotherm peaks	316.5, 338	(4)
		DSC, dual endotherm peaks		(7)
		35% mmmm	324, 339	
		40% mmmm	326, 337	
		DSC endotherm peak range	427–433	(1)
Heat of fusion (experimental)	$kJ\,mol^{-1}$	DSC, >20 polymers (10–70 $J\,g^{-1}$)	0.4–2.9	(2)
		DSC, 45-54% mmmm (31–40 $J\,g^{-1}$)	1.3–1.7	(6)
		DSC, 40% mmmm (14 $J\,g^{-1}$)	0.59	(7)
Crystallinity	%	DSC		(6)
		54% mmmm	19.1	
		45% mmmm	14.8	
		52% mmmm	16.7	
		DSC (ELPP type of reference (8))	13	(4)
		XRD	16	(4)
		Annealed, XRD, 30°C, 35-40% mmmm	26–27	(9)
		XRD, density methods, fractionated ELPP		(10)
		Whole ELPP, IV = 2.7 $dl\,g^{-1}$, XRD (density)	21 (19)	
		Ether soluble, 0.73 $dl\,g^{-1}$	8 (0)	
		Hexane soluble, 2.56 $dl\,g^{-1}$	14 (17)	
		Hexane insoluble, 4.16 $dl\,g^{-1}$	29 (44)	
		Whole ELPP, IV = 12.1 $dl\,g^{-1}$	17 (24)	
		Ether soluble, 3.42 $dl\,g^{-1}$	9 (9)	
		Hexane soluble, 7.80 $dl\,g^{-1}$	15 (25)	
		Hexane insoluble NA	22 (29)	
Equilibrium modulus	MPa	50°C, 0.5% strain, stress relaxed 10^4 s (2 examples)	0.56 1.47	(7)
Segment length between virtual cross-links	Daltons	M_n of amorphous segments between physical cross-links, estimated from $M_{n,a}$ = density × RT/G_{eq} (2 examples)	2,100 4,400	(7, 9)
		Mechanical rheometry, 25°C	940	(11)
Tensile strength	MPa	51 $cm\,min^{-1}$, ASTM D-412	5–8	(2)
		51 $cm\,min^{-1}$	3.2	(5)
		25.5 $cm\,min^{-1}$	16–39	(6)
		20 $cm\,min^{-1}$	4–12	(7, 9, 12)
		10 $mm\,min^{-1}$, some necking	22	(13)
		51 $cm\,min^{-1}$	11.7–14.8	(14)
		51 $cm\,min^{-1}$, syndiotactic ELPP	11	(15)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Maximum extensibility	%	51 cm min^{-1}	>1,000	(2)
		51 cm min^{-1}	1,200	(5)
		25.5 cm min^{-1}	800	(6)
		20 cm min^{-1}	525–1,260	(7, 9, 12)
		10 mm min^{-1}, some necking	700	(13)
		51 cm min^{-1}	814–863	(14)
		51 cm min^{-1}, syndiotactic ELPP	750–908	(15)
		Not specified	>1,000	(1)
Tensile modulus	MPa	DIN 53457, 23°C	23–28	(3)
		Not specified	69–359	(1)
		51 in min^{-1}	1.7	(5)
Impact strength	kJ m^{-2}	Tensile impact, ISO 8256, 23°C	270–300	(3)
		Flexural impact, ISO 179 1 eu, −20°C	14–22	
Hardness	°Shore	Shore A	77–83	(3)
			81–96	(1)
Tensile set	%	300% extension, 51 cm min^{-1}, ASTM D412, 23°C, no hold at extension	80	(3)
			93	(2)
			60–130	(16)
			50	(5)
			82–93	(14)
			22–28	(15)
		300% extension, 20 cm min^{-1}, no hold at extension	24	(7, 9, 12)
		300%, conditions not specified	100–200	(1)
		400% extension, 51 cm min^{-1}, no hold at extension	65–110	(15)
Tensile recovery	%	100% extension, 25.5 cm min^{-1}	92–97	(6)
		No hold at extension, 2 min recovery after extension	97	(7, 9, 12)
		200% extension, 25.5 cm min^{-1}	90–97	(6)
		No hold at extension, 2 min recovery after extension	96	(7, 9, 12)

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Polypropylene, isotactic

DAVID V. HOWE

ACRONYM PP

CLASS Poly(α-olefins)

STRUCTURE

$$\begin{array}{c} \quad\;\; CH_3 \\ \quad\;\; | \\ [-CH_2CH-] \end{array}$$

MAJOR APPLICATIONS Fiber, slit tape, cast and biaxially oriented film, containers and closures, automotive interior trim, appliance housings and components, component in elastomeric blends with polyethylene and olefinic rubbers.

PROPERTIES OF SPECIAL INTEREST Low cost; easily processed by injection molding, extrusion, and spinning; can be oriented; excellent resistance to chemicals; low color; can be stabilized to provide good thermal aging stability; moderate strength and stiffness; good toughness when impact modified either in the reactor or by compounding; excellent flexural fatigue resistance; modest clarity.

PREPARATIVE TECHNIQUES Ziegler-Natta polymerization with titanium halide/ aluminum alkyl catalyst and, optionally, ether, ester, or silane activator. Catalyst may be deposited on a magnesium chloride support. Slurry and gas phase processes are used. Catalyst systems based on metallocenes are under development. Typical comonomers are ethylene and 1-butene.

Isotacticity

Polymerization Conditions	Isotacticity				Reference
	Isotactic index (% heptane insolubles)	Xylene insolubles	% mmmm	% mm	
$MgCl_2/TiCl_4$/DIBP* catalyst modified with TMPIP* and $AlEt_3$ prepared at 140°C	–	94	89.3	–	(1)
$MgCl_2/TiCl_4$/DIBP* catalyst modified with (i-Bu)$_2$Si(OMe)$_2$) and AlEt3	97	–	–	–	(2)
$MgCl_2/TiCl_4$/DE* catalyst modified with $AlEt_3$	95–99	–	–	–	(3)
Various $MgCl_2$ or $TiCl_3$ supported Ziegler-Natta catalysts	–	–	–	92.2–94.9	(4)

*DIBP = Diisobutyl phthalate; TMPIP = 2,2,6,6-tetramethylpiperidine; DE = 1,3-diether.

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Molecular weight (M_w) and polydispersity index (M_w/M_n)

Polymerization conditions	M_w (g mol^{-1})	M_w/M_n	Reference
$MgCl_2/TiCl_4$/DIBP catalyst modified with (*i*-Bu) $_2Si(OMe)_2$) and $AlEt_3$			(2)
H_2 concentration = 0 mol l^{-1}	560,000	3.8	
H_2 concentration = 6.9×10^{-3} mol l^{-1}	382,000	6.1	
Typical range (extrapolated from melt flow rates of commercial products)	<100,000–>600,000	5–12	(5, 6)
Borealis VC20 82C (MFR: 20 g/10 min)	265,000	4.3	(7)
Typical for controlled rheology (chemically cracked products)	–	<5	(8, 9)
Single site catalyst	–	~2	(10)
Melt flow index			(5)
0.63	646,000	–	
2.9	412,000	–	
11.9	297,000	–	

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight of repeat unit	g mol^{-1}	$-CH_2-CH(CH_3)-$	42.07	
Morphology (blends, 'impact copolymer')	–	Elastomer content <~60%	Dispersed phase	(11)
		Elastomer content >~60% (depends upon processing conditions)	Dispersed or co-continuous phase	
IR (characteristic absorption frequencies)	cm^{-1}	CH_3, CH_2, CH stretching	2956 (s), 2951 (s), 2925 (sh), 2907 (sh), 2880 (s), 2868 (s), 2843 (s)	(12, 13)
		CH_3 antisymmetric bending, CH_2 bending	1459 (sh), 1454 (s)	
		Various CH_3, CH_2, and CH bending, wagging, twisting, C–C stretching	1377 (s), 1359 (m), 1329 (w), 1305 (w), 1297 (w), 1257 (w), 1219 (w)	
		Various CH_3, CH_2, and CH bending, wagging, twisting, and rocking, C–C stretching	1167 (s), 1153 (sh), 997 (s), 973 (s), 841 (s), 809 (m)	
NMR		^1H NMR		(14–17)
		^{13}C NMR		(18, 19)
Coefficient of linear thermal expansion	K^{-1}	ASTM Method D696		(20)
		From 243 to 273 K	6.5×10^{-5}	
		From 273 to 303 K	1.05×10^{-4}	
		From 303 to 330 K	1.40×10^{-4}	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Coefficient of thermal expansion (volume, melt)	K^{-1}	From 448 to 573 K	6.6×10^{-4}	(21)
		From 453 to 503 K	6.7×10^{-4}	(22)
Isothermal compressibility	bar^{-1}	453 K	1.27×10^{-4}	(22, 23)
		493 K	1.5×10^{-4}	
		533 K	1.78×10^{-4}	
Density	$g\,cm^{-3}$	298 K, α-crystalline phase	0.936–0.946	(24, 25, 26)
		298 K, amorphous phase	0.850–0.855	
		298 K, typical commercial material	0.90–0.91	
Solvents		Room temperature	No common solvents	(27)
Solubility parameter	$(MPa)^{1/2}$	Inverse phase gas chromatography	18.8	(28)
		Montell Profax 6701	17.3	(29)
Theta temperature	K	M_w = 28,000–564,000		(30, 31)
		p-tert-amylphenol	414	
		dibenzyl ether	456	
		biphenyl	398	
		n-butanol	420	
Lattice	—	α_1, α_2-forms	Monoclinic	(24, 32)
		β-form	Hexagonal	(32)
		γ-form	Orthorhombic	(32, 33, 34)

Form	Space group	Chain conformation	Unit cell dimension (Å)			Unit cell angle (degrees)	Conditions	Reference
			a	*b*	*c*			
α_1	C_1/c	Helix (3/1)	6.67	20.8	6.50	98.67	Oriented, annealed 413 K	(35)
α_2	$P2_1/c$	Helix (3/1)	6.65	20.73	6.50	98.67	Oriented, annealed 443 K	(35)
β	$P3_121$	Helix (3/1)	11.03	11.03	6.49	—	—	(32)
γ	Fddd	Helix (3/1)	8.54	9.93	42.41	—	—	(32, 33, 34)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of fusion	$J\,g^{-1}$	DSC, α-crystalline material (100%)	165	(25)
Degree of crystallinity	%	DSC, density depends upon tacticity and crystallization conditions	50–70	(4, 7, 26)
Glass transition temperature	K	DMA		(7)
		30 Hz	283.7	
		1 Hz	275.5	
Melting point	K	100% crystalline	~459	(36)

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Commonly reported mechanical properties*

PROPERTY	UNITS	CONDITIONS	POLYMER TYPE			
			IPP[(a)]	RCP[(b)]	IPC-L[(c)]	ICP-H[(c)]
Yield stress	MPa	ASTM D638	34.5	27.6	26.2	22.0
Yield strain $(L/L_0)_y$	%	ASTM D638	10	14	12	14
Flexural modulus	MPa	ASTM D790	1,389	1,035	1,210	1,000
Izod impact strength[(d)]	$J\ m^{-1}$	ASTM D256	27	55	130	No break
Hardness	Rockwell	ASTM D785	R90	R80	R80	R60
Deflection temperature	K	ASTM D648, 0.45 MPa outer fiber stress	380	360	360	345

* These are typical properties for the classes of materials based on the range of properties reported in references (37) and (38).
(a) IPP = isotactic propylene homopolymer.
(b) RCP = ethylene-propylene random copolymer with an ethylene content of about 3%.
(c) ICP = blends of isotactic propylene homopolymer with ethylene-propylene rubber. These materials are commonly called "impact copolymers," "heterophasic copolymers," or, incorrectly, "block copolymers." These are typically prepared during the polymerization process using a series of reactors. L = low rubber (less than about 15% rubber by weight; typically with an ethylene content of less than about 10%). H = high rubber content blends (greater than about 15% rubber by weight; typically with an ethylene content of at least 7%).
(d) Impact strength is very dependent upon the molecular weight of the polymer as well as the rubber content of the material. These data are for typical injection molding grade materials.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Storage modulus	MPa	293 K, Homopolymer, 30 Hz	1,400	(7)
Tan δ	—	293 K, Homopolymer, 30 Hz	0.086	(7)
Poisson ratio	—	296 K	0.38	—
Index of refraction n_D	—	293 K, density 0.9075 $g\ cm^{-3}$	1.5030	(39)
Refractive index Increment dn/dc	—	1-Chloronaphthalene and 1,2,4-trichlorobenzene solvents	(*see reference*)	(40)
Dielectric constant ε'	—	At 1 KHz (D150) At 1 MHz	2.2-2.3 2.1-2.3	(26) (41)
Dielectric strength	$V\ cm^{-1}$	298 K (D149) 298 K 393 K	240,000 217,000–300,000 170,000	(26) (41) (26)
Dissipation factor	—	60 Hz–100 MHz (D510) 1 MHz	0.3–1 $(\times 10^{-3})$ 1–3 $(\times 10^{-4})$	(26) (41)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Volume resistivity	ohms cm	ASTM D257	10^{16}–10^{17}	(26, 41)
Surface tension γ	mN m^{-1}	438 K 473 K 495 K	22.5 21.2 20.2	(42) (43) (42)
Surface free energy	mJ m^{-2}	298 K (calculated from advancing contact angles)	29.0	(43)
Contact angle	degrees	H_2O; advancing, 298 K CH_2I_2; advancing, 298 K	116 64	(43)
Permeability coefficient	m^3(STP) m s^{-1} m^{-2} Pa^{-1}	H_2O, 298 K O_2, 298 K (isotropic, all presures) O_2, 298 K (12.5 : 1 draw ratio) CO_2, 298 K (<1 atm) CO_2, 298 K (50 atm)	3.83×10^{-16} 7.73×10^{-18} 2.12×10^{-18} 2.37×10^{-17} 7.50×10^{-17}	(44) (45) (45) (46) (46)
Thermal conductivity	W m^{-1} K^{-1}	293 K	0.12 0.22	(47)
Melt flow rate	g (10 min) $^{-1}$	ASTM D1238, 503 K, 2.16 kg	0.2–>500	–
Speed of sound	m s^{-1}	Unoriented 298 K 398 K Oriented Long. dir. 298 K Trans. dir. 298 K	 2.5×10^3 125×10^3 3.3×10^3 2.1×10^3	(48) (49)
Decomposition temperature	K	TGA in helium, Montell Profax 6501	623	(50)
Ignition temperature	K	Calculated from critical heat flux data	736	(51)
Oxygen index	%	ASTM D2863, Montell Profax 6505	17.4	(52)
Scission, G factor	–	γ irradiation Initial At doses above gel point	 1.2 0.27	(53, 54)
Cross-linking, G factor	–	γ irradiation	0.07-0.30	(53, 54)
Producers	–	Worldwide in 1994 (see table below for examples)	~117	(55)
Capacity	ktons	Worldwide in 1994 (see table below for examples)	20,492	(55)

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Some producers and capacities (from 1996)[56]

Producer	Capacity (ktons)
Montell, Hoofddrop, The Netherlands	3,034
Targor, Mainz, Germany	1,370
Amoco, Chicago, USA	1,183
Japan Polychem, Tokyo, Japan	1,103
Fina, Brussels, Belgium	1,030

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Poly(propylene oxide)

QINGWEN WENDY YUAN

ACRONYM PPO

CLASS Polyethers

STRUCTURE $[-CH_2-CH(CH_3)-O-]$

PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–			59	–
Polymerization	–	–			Ring-opening	(1)
Typical copolymers	Ethylene oxide-propylene oxide copolymer					(2)
Solvents	Benzene, ethanol, dioxane, chloroform, tetrahydrofuran, methanol (hot), acetone					(3)
Nonsolvent	Diethyl ether (sw), 2-aminoethanol, ethyl acetate (sw), N,N-dimethylacetamide					(3)
Theta temperature	K	Iso-octane, virial coefficients			323.5	(3, 4)
Second virial coefficient	$mol\,cm^3\,g^{-2}$	Solvent	Temp. (°C)	Mol. wt. ($g\,mol^{-1}$)		
		Acetone	25	0.067×10^{-3}	-90×10^{-4}	(3, 5)
				0.125×10^{-3}	0	(3, 5)
				$(0.45–3.85) \times 10^{-3}$	$\sim 15.2 \times 10^{-4}$	(3, 5)
		Hexane	46	$(783–901) \times 10^{-3}$	$(0.46–4.50) \times 10^{-4}$	(3, 4)
				$(34.2–4{,}410) \times 10^{-3}$	$(3.16–0.523) \times 10^{-4}$	(3, 6)
		Methanol	20	$(0.535–3.31) \times 10^{-3}$	$(10.75–0.95) \times 10^{-7}$	(3, 7)
		Iso-octane	48–85	901×10^{-3}	$(0–1.58) \times 10^{-4}$	(3, 4)
			50–89	783×10^{-3}	$(-0.25$ to $1.72) \times 10^{-4}$	(3, 4)

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PROPERTY	UNITS	CONDITIONS			VALUE		REFERENCE
Mark-Houwink parameter: K and a	$K = \mathrm{ml\,g^{-1}}$ $a =$ None	Solvent	Temp. (°C)	Mol. wt. ($\mathrm{g\,mol^{-1}}$)	K ($\times 10^{-3}$)	a	
		Acetone	25	$(0.1–0.4) \times 10^4$	75.5	0.56	(3, 8)
		Benzene	20	$(0.07–0.33) \times 10^4$	11.1	0.79	(3, 9)
			25	$(3–70) \times 10^4$	11.2	0.77	(3, 6)
				—	14	0.8	(3)
		Isotactic:					
		Benzene	25	$(0.5–92) \times 10^4$	38.5	0.73	(3, 10)
				$(1–8) \times 10^4$	41.3	0.64	(3, 11)
				$(0.05–0.4) \times 10^4$	41.5	0.65	(3, 8)
		Hexane	46	$(3.4–367) \times 10^4$	19.7	0.67	(3, 6)
		Methanol	20	$(0.05–0.33) \times 10^4$	40.6	0.64	(3, 9)
			25	$(1–7) \times 10^4$	76.9	0.55	(3, 11)
		Tetrahydrofuran	20	$(0.05–0.33) \times 10^4$	55.0	0.62	(3, 9)
			25	$(3–70) \times 10^4$	12.9	0.75	(3, 9)
		Toluene/2,2,4-trimethylpentane (5/7 vol)	39.5	$(1–7) \times 10^4$	107.5	0.50	(3, 6)
		Oligomer:					
		Acetone	20	$(0.1–0.4) \times 10^4$	75.5	0.56	(3, 12)
		Benzene	20	$(0.04–0.4) \times 10^4$	41.5	0.65	(3, 12)
Heat of solution	$\mathrm{J\,g^{-1}}$	Above glass transition					(3)
		Carbon tetrachloride, 30°C, $6 \times 10^4\,\mathrm{g\,mol^{-1}}$			−20		
		Chloroform, 30°C, $6 \times 10^4\,\mathrm{g\,mol^{-1}}$			−100		
		Methyl alcohol, 27°C, $10^3\,\mathrm{g\,mol^{-1}}$			−7		
Glass transition temperature	K	Conflicting data			198		(3)
		Amorphous, atactic			201.5		(2)
		Method: dynamic mechanical spectrum:					(13)
		PPO cross-linked with stoichiometric quantities of tris(p-isocyanatophenyl-thiophosphate)					
		$M_c = 452\,\mathrm{g\,mol^{-1}}$			328.3		
		$M_c = 725\,\mathrm{g\,mol^{-1}}$			281.3		
		$M_c = 1{,}025\,\mathrm{g\,mol^{-1}}$			262.6		
		$M_c = 2{,}000\,\mathrm{g\,mol^{-1}}$			241.0		
		$M_c = 3{,}000\,\mathrm{g\,mol^{-1}}$			235.6		
		PPO cross-linked with stoichiometric quantities of an aromatic triisocyanate					
		$M_c = 425\,\mathrm{g\,mol^{-1}}$			321.1		
		$M_c = 725\,\mathrm{g\,mol^{-1}}$			277.6		
		$M_c = 1{,}025\,\mathrm{g\,mol^{-1}}$			265.8		
Melting temperature	K	Isotactic			348.5		(2)

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PROPERTY	UNITS	CONDITIONS			VALUE		REFERENCE
Heat capacity	$kJ\,K^{-1}\,mol^{-1}$ $(\times 10^{-3})$	Temp. (K)			Solid	Melt	(3, 13)
		80			31.21	–	
		90			34.33	–	
		100			37.37	–	
		110			40.34	–	
		120			43.22	–	
		130			46.03	–	
		140			48.76	–	
		150			51.41	–	
		160			53.98	–	
		170			56.48	–	
		180			58.89	–	
		190			61.23	–	
		200			–	95.46	
		210			–	97.04	
		220			–	98.61	
		230			–	100.19	
		240			–	101.77	
		250			–	103.35	
		260			–	104.92	
		270			–	106.50	
		280			–	108.08	
		290			–	109.65	
		300			–	111.23	
		310			–	112.81	
		320			–	114.38	
		330			–	115.96	
		340			–	117.54	
		350			–	119.12	
		360			–	120.69	
		370			–	122.27	
Index of refraction	–	–			1.4495		(3)
Specific refractive index increment dn/dc	$ml\,g^{-1}$	Solvent	Temp. (°C)	Mol. wt. ($g\,mol^{-1}$)	$\lambda_0 = 436\,nm$	$\lambda_0 = 546\,nm$	
		Acetone	25	67	0.085	–	(5)
				125	0.0915	–	(5)
				450	0.096	–	(5)
				1,100	0.099	–	(5)
				1,200	0.099	–	(5)
				2,100	0.100	–	(5)
				3,270	0.100	–	(5)
				3,850	0.101	–	(5)
		Benzene	25	–	−0.0530	−0.0448	(6)
		Chlorobenzene	25	–	−0.0658	0.0638	(6)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE

Specific refractive index increment dn/dc (units: ml g^{-1})

Solvent	Temp. (°C)	Mol. wt. ($g\,mol^{-1}$)	$\lambda_0 = 436\,nm$	$\lambda_0 = 546\,nm$	Reference
n-Hexane	25	–	0.0775	0.0775	(6)
	40	–	0.0460	0.0460	(6)
	46	9.6×10^5	0.0887	0.0887	(6)
		2.0×10^5	0.0895	0.0895	(6)
	57	9.6×10^5	0.101	0.101	(6)
	57	2.0×10^5	0.0104	0.0104	(6)
Feron 113	25	–	0.118	0.115	(6)
Iso-octane	35	–	0.0655	0.0655	(6)
Methanol	24	–	0.137	0.135	(3)
	25	12.2×10^5	0.118	0.118	(6)
		12.5×10^5	0.115	0.115	(6)

Property	Units	Conditions	Value	Reference
Dipole moment	D	Benzene, $T = 25°C$, $P_n = 6.6–69.0$	1.40–1.02	(3, 14)

Surface tension (units: mN m^{-1}), reference (3)

Conditions	20°C	150°C	200°C
Diol, $M = 2,025\,g\,mol^{-1}$	31.5	21.1	17.1
Diol, $M = ?$	31.7	20.6	16.4
Diol, $M = 3,000\,g\,mol^{-1}$	31.2	20.9	17.0
Diol, $M = 400–4,100\,g\,mol^{-1}$	31.1	21.6	17.9
Poly(oxypropylene)-dimethylether, $M = 3,000\,g\,mol^{-1}$	30.7	18.3	13.6

Diffusion coefficient (units: $cm^2\,s^{-1}$ ($\times 10^{-7}$)), reference (3)

Solvent	Temp. (°C)	Mol. wt. ($g\,mol^{-1}$)	Value
Acetone	20	$(0.074–3.375) \times 10^3$	$D_0 = K_s \times M^{-0.52}$
Benzene	20	$(0.134–3.375) \times 10^3$	$D_0 = K_s \times M^{-0.55}$
Water	25	40×10^3	3.73
		73×10^3	2.09
		148×10^3	1.66
		278×10^3	1.72
		661×10^3	1.07
	15	148×10^3	1.73
	34	–	2.47
	43	–	2.88
	30.3	–	2.72
	35.4	–	3.08
	40.5	–	3.25
	45.5	–	3.49

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Permeability coefficient	$m^3\ m\ s^{-1}\ m^{-2}\ Pa^{-1}$ $(\times 10^{-19})$	PPO cross-linked with stoichiometric quantities of tris(*p*-isocyanatophenyl-thiophosphate)	H_2	CO	(3, 15, 16)
		$M_c = 425$	2.86	0.0608	
		$M_c = 725$	7.26	0.65	
		$M_c = 1,025$	18.80	2.93	
		$M_c = 2,000$	28.73	7.65	
		$M_c = 3,000$	44.10	12.60	

Crystalline-state properties[3]

Lattice	Space group	Unit cell parameters (Å)			Monomers per unit cell	Density (g cm^{-3})	Heat of Fusion (kJ mol^{-1})
		a	*b*	*c*			
Orthorhombic	C2V-9 or D2-4	10.52	4.67	7.16	4	1.097	8.4
Orthorhombic	D2-4	10.51	4.69	7.09	4	1.104	
Orthorhombic	D2-4	10.52	4.68	7.10	4	1.104	
Orthorhombic	D2-4	10.40	4.64	6.92	4	1.155	
Orthorhombic	D2-4	10.46	4.66	7.03	4	1.126	

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Poly(propylene sulfide)

JUNZO MASAMOTO

ACRONYM PPS

CLASS Polysulfides

STRUCTURE $-[CH(CH_3)S]_n-$

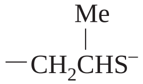
MAJOR APPLICATIONS Poly(propylene sulfide) is an elastic material that compares with styrene-butadiene rubbers. However, this polymer has not yet achieved commercial production, although the PPS elastomer offers a combination of good solvent and weather resistance. Low molecular weight functional PPS is suitable for use in sealants, adhesive, etc.[1]

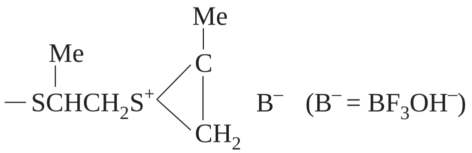
PROPERTIES OF SPECIAL INTEREST Poly(propylene sulfide) is an elastic material with an excellent combination of good solvent- and weather-resistance with an acceptable level of physical and dynamic properties. It also gives both types of crystalline stereoregular polymer and amorphous atactic polymer depending on the initiator.[2] By using an optically active coordination initiator, an isotactic optically active polymer can be obtained.[3–7]

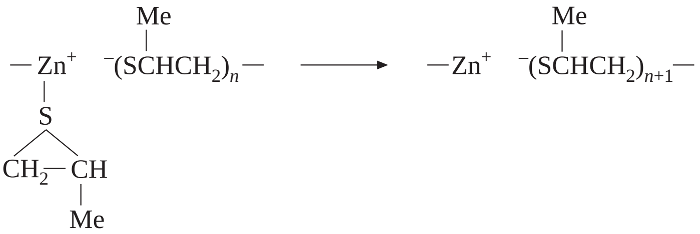
OTHER POLYMERS SHOWING THESE SPECIAL PROPERTIES Solvent resistance: polysulfide rubbers; second order transition temperature: styrene-butadiene rubbers; weather and ozone resistance: polychloroprene rubbers.

PREPARATIVE TECHNIQUE Poly(propylene sulfide) can be prepared by ring-opening polymerization, using anionic, cationic, and coordinate catalyst. Anionic and cationic systems give an amorphous atactic polymer, while coordinate catalytic system, such as cadmium salts, give an isotactic or crystalline polymer.[2,8]

The monomer undergoes polymerization by an anionic mechanism with basic initiators:[1]

(Anionic) 

(Cationic) 

(Coordinate) 

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The cationic polymerization by initiators such as boronfluoride, etherate, probably involves the intermediary of sulphonium ions:[1] In polymerization initiated by zinc or cadmium compounds, the metal-sulfur bond will be predominantly covalent, and it is possible that the monomer is coordinated to the metal atom before insertion into the growing chain.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	74	—
Tacticity (stereoregularity)	%	Coordination polymerization, cadmium thiolate catalyst	Isotactic: 90–100 meso dyads	(6, 9–11)
		Anionic polymerization, sodium thiolate active center	Atactic	(10)
		Zinc N-substituted porphyrins	Atactic	(12)
Typical molecular weight range of polymer	$g\,mol^{-1}$	Anionic polymerization, active center: sodium thiolates; determined by osmotic pressure method	M_n: $1–6 \times 10^5$	(13)
		For amorphous PPS, in toluene solution at 35°C	Intrinsic viscosity 0.5–3.0	(8)
		In benzene solution at 25°C, $ZnEt_2/H_2O$, cadmium tartrate initiator	Intrinsic viscosity 2.0–4.0	(14)
		For crystalline PPS, in toluene solution at 35°C	Intrinsic viscosity 0.5–2.5	(8)
		KSCN initiator with a cryptate	M_w: 1.7×10^7	(15)
		Rare earth coordination catalyst	M_w: $1–5 \times 10^6$	(16)
		Initiator: zinc N-substituted porphyrins	M_n: $1–27 \times 10^3$	(12)
		Initiator: cadmium thiolate	M_n: $3–15 \times 10^4$	(7)
Typical polydispersity index (M_w/M_n)	—	Anionic polymerization; active center: sodium thiolates, tetrahydrofuran solvent	1.1–1.2	(13)
		Anionic polymerization; initiator: sodium naphthalene, tetrahydrofuran solvent	<1.1	(17)
		Initiator: zinc N-substituted porphyrins	1.05	(11)
		Initiator: cadmium crotyl mercaptide, M_w: $(1.1 \sim 15.8) \times 10^4$	$1.7 \sim 2.3$	(18)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
IR (characteristic absorption frequencies)	cm	$-CH_2-$ deformation	1,449	(8)
		Symmetrical $-CH_3$ deformation	1,379	
		Asymmetrical –C–S– stretching vibration	735	
		Symmetrical –C–S– stretching vibration	684	
NMR	^{1}H NMR, 300-MHz NMR at 17°C in deutrated chloroform or carbon tetrachloride			(19)
	^{13}C NMR, operating at 25 MHz in CCl_4–C_6D_6			(9)
	(90/10) at 160°C or at 60°C			(12)
Thermal expansion coefficients	K^{-1}	Atactic PPS, $M_w = 5 \times 10^5$	0.59×10^{-3}	(20)
Density (amorphous)	$g\,cm^{-3}$	At 25°C, by pyconometry measurement	1.0340	(20)
			1.130	(8)
Solvents	(Cyclic) propylene sulfide			(20)
	Benzene, tetrahydrofuran, toluene, carbon tetrachloride, *o*-dichlorobenzene			(8)
Nonsolvents	–	For atactic PPS	Methyl ethyl ketone	(21)
		For crystalline PPS	Heptane, cyclohexane, dibutylphthalate, aqueous hydrochloric acid, aqueous sodium hydroxide	(8)
Solubility parameter	MPa	–	17.9	(21)
Mark-Houwink parameters: *K* and *a*	$K = ml\,g^{-1}$	Benzene, 20°C	$K = 3.3 \times 10^{-5}$; $a = 0.86$	(23)
	a = None	Benzene, 31°C	$K = 5.036 \times 10^{-5}$; $a = 0.78$	(18) (24)
		Tetrahydrofuran, 25°C	$K = 2.58 \times 10^{-4}$; $a = 0.656$	
Characteristic ratio $\langle r^2 \rangle / nl^2$	–	Atactic PPS	4.0	(25)
Lattice	–	–	Orthorhombic	(21)
Space group	–	–	$P2_12_1$-D_24	(21)
Chain conformation	–	–	Planar zigzag (but not fully extended)	(21, 24)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Unit cell dimensions	Å	X-ray photograph of oriented samples of both types of optical active and racemic PPS; both: isotactic	$a = 9.95$, $b = 4.89$, $c = 8.20$ (fiber axis)	(21)
Unit cell contents	–	–	4 monomeric units per unit cell (2 molecular chains)	–
Degree of crystallinity	%	Initiator: Zn/H_2O, DTA and X-ray diffraction	60	(14)
		Initiator: cadmium tartrate, DTA and X-ray diffraction	85	
Density	$g\ cm^{-3}$	Theoretical density for crystalline PPS	1.24	(21)
		Observed density for crystalline PPS	1.152	(21)
		–	1.16	(8)
Glass transition temperature	K	–	220.5	(27, 28)
		Amorphous and crystalline PPS	225	(8)
			233	(29)
		Sulfur-vulcanized carbon black filled propylene sulfide-allyl thioglycidil ether copolymer prepared by coordination catalyst	233	(2)
		Viscoelastic measurement	234.6	(29)
		Calorimetric	236	(31)
Melting point	K	Isotactic PPS	313–314	(8)
			325	(9)
		Calorimetric, Et_2Zn-S catalyst	326	(30)
		Isotacticity: >90%	331	(7, 14)
Tensile strength	MPa	Sulfur-vulcanized PPS-allyl thioglycidyl ether copolymer filled with carbon black	11	(2)
		Sulfur-vulcanized ethylene sulfide (28 mol%), propylene sulfide (69 mol%), allyloxymethyl thiarne (3 mol%), terpolymer filled with carbon black	15.9	(8)
		PPS homopolymer filled with carbon black	13	(1)
		PPS homopolymer, cured without carbon black	1.2	(1)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Maximum extensibility (elongation)	%	Sulfur-vulcanized PPS-allyl thioglycidyl ether copolymer filled with carbon black	225	(2)
		Sulfur-vulcanized ethylene sulfide propylene sulfide allyloxymethyl thiarne terpolymer filled with carbon black	360	(8)
		PPS filled with carbon black	205	(1)
		PPS cured without carbon black	325	(1)
Hardness	Shore A	Sulfur-vulcanized PPS-allyl thioglycidyl ether copolymer filled with carbon black	80	(2)
		Sulfur-vulcanized ethylene sulfide propylene sulfide allyloxymethyl thiarne terpolymer filled with carbon black	81	(8)
		PPS filled with carbon black	76–70	(1)
		PPS cured without carbon black	38–30	(1)
Modulus	MPa	Modulus at glassy state: viscoelastic method	2200	(31)
		Modulus at rubbery state: viscoelastic method	4.3	(31)
		At 300% elongation, sulfur-vulcanized ethylene sulfide propylene sulfideallyloxymethyl thiarne terpolymer filled with carbon black	13.8	(8)
		At 100% elongation, PPS filled with carbon black	5.8	(1)
		At 100% elongation, PPS cured without carbon black	0.55	(1)
Rebound	%	PPS filled with carbon black	54	(1)
Entanglement molecular weight	$g\ mol^{-1}$	M_w: $0.3–86 \times 10^4$	2×10^4	(18)
Index of refraction	–	–	1.596–1.597	(30)
		At 23°C	1.594	(18)
Refractive index increment dn/dc	$ml\ g^{-1}$	–	8.095×10^{-2}	–
Dipole moment ratio $\langle \mu^2 \rangle / nm^2$	–	In benzene at 25°C, isotactic PPS	0.39	(10)
		In benzene at 25°C, atactic PPS	0.44	
		In carbon tetrachloride at 25°C, isotactic PPS	0.33	
		In carbon tetrachloride at 25°C, atactic PPS	0.37	
Melt viscosity	Pa s	For M_w =		(18)
		7,000 at 30°C	0.006	
		15,000	0.03	
		29,000	0.2	
		60,000	1.6	
		118,000	15.8	
		158,000	54.7	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Weathering test	—	In Toronto, one year's exposure; sulfur-vulcanized ethylene sulfide propylene sulfide allyloxymethyl thiarne terpolymer filled with carbon black	No outward change	(8)
Solvent resistance	% volume swell	7 days at room temperature; sulfur-vulcanized propylene sulfide-allyl thioglycidyl ether copolymer filled with carbon black		(2)
		Ethyl acetate	75	
		Methyl ethyl ketone	101	
		Hexane	10	
		Toluene	173	
Availability		No commercial production		

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Polypropylene, syndiotactic

CHARLES L. MYERS

ACRONYMS s-PP, sPP

CLASS Poly(α-olefins)

STRUCTURE $-[CH_2CHCH_3]-$

MAJOR APPLICATIONS Produced for several years in developmental quantities and in commercial scale tests. Being evaluated in various forms (homopolymer, impact copolymer) for molding and film applications. See references (1, 2 , 3, 4).

PROPERTIES OF SPECIAL INTEREST Transparency, flexibility, toughness, heat seal temperature, radiation stability, and low extractables.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	Unit cell, 100% crystalline (obsolete cell interpretation)	0.93	(5)
		25°C, experimental sample not defined	0.989–0.91	(5)
		25°C, amorphous, extrapolated from melt temperature	0.856	(5)
		Three s-PP (Fina)		(2, 6)
		% r / % rrrr / % crystallinity XRD		
		91.4 / 76.5 / 21	0.87	
		91.9 / 78.0 / 22	0.87	
		96.5 / 91.1 / 29	0.89	
		Two s-PP (Hoechst)		(3)
		G 1	0.887	
		G 2, 83.6% rrrr, 27% crystalinity	0.885	
Melting temperature	K	rrrr = 72%	392	(7)
		rrrr = 82%	413	
		Three s-PP (Fina)		(2, 6)
		% r / % rrrr / % crystallinity		
		91.4 / 76.5 / 21	398	
		91.9 / 78.0 / 22	399	
		96.5 / 91.1 / 29	421	
		G 2 (Hoechst), 83.6% rrrr	406	(3)
Melting temperature (equilibrium values, Hoffmann-Weeks)	K	rrrr = 92–95%	433–459	(8)
		r = 94%, rrrr = 86%, $M_n > 40{,}000$	433	(9)
		r = 96.8%, rrrr = 92.1%, $M_w = 164{,}000$	439	(10)
		r = 91.9-98.0%, rrrr = 81.4–94.5%	408–459	(10)
		–	424–428	(11)
		Extrapolated to 100% syndiotacticity	487	(10)
		–	493	(12)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of fusion (equilibrium values, for 100% crystallinity)	$kJ\,mol^{-1}$	rrrr = 92-95%	4.4–8.2	(8)
		r = 94%, rrrr = 86%, $M_n > 40{,}000$	8.0	(9)
		r = 96.8%, rrrr = 92.1%, $M_w = 164{,}000$	6.9	(10)
		—	8.4	(11)
Entropy of fusion	$J\,K^{-1}\,mol^{-1}$	DSC, density	18.8	(13, 14)
Theta temperature	K	$M_w = 11{,}700$, cyclohexane	309	(15, 16)
Infrared absorption	cm^{-1}	Attributed to		(2, 5)
		Helix	866, 867	
		Helix	977	
		Regularity	962	
Flexural modulus	MPa	Three s-PP (Fina)		(2, 6)
		% r / % rrrr / % crystallinity		
		91.4 / 76.5 / 21	380	
		91.9 / 78.0 / 22	415	
		96.5 / 91.1 / 29	760	
		Homopolymer	359	(1)
		Clear, impact grades	88–250	(1)
		Two s-PP (Hoechst)		(3)
		G 1	790	
		G 2, 83.6% rrrr	600	
Tensile modulus	MPa	Homopolymer	483	(1)
		Clear impact grades	211–244	
Tensile elongation, yield	%	Homopolymer	10.8	(1)
Tensile elongation, break	%	Homopolymer	180	(1)

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Polypropylene, syndiotactic

Unit cell information

Comments	Lattice	Packing	Momomers per unit cell	Cell dimensions (Å) a	b	c	Space group	Crystal density	Reference
Type III High order	Orthorhombic	Helical Antichiral	16	14.5	11.2	7.4	*Ibca*	—	(9, 17–20)
Type II Disorder	Orthorhombic	Helical Antichiral	8	14.5	5.6	7.4	$Pca2_1$	—	(9, 17–19)
Type I Annealed fiber (high order structure in older literature)	Orthorhombic	Helical Isochiral	8	14.5	5.6	7.4	$C222_1$	0.93 0.90	(5, 9, 17–19)
Quenched, cold drawn, unstable	Orthorhombic	Planar Zigzag	4	5.22	11.17	5.06	$P2_1cn$	0.945	(5, 9, 20, 21)
Unstable	Triclinic	Deformed helix or intermediate	6	5.72	7.64	11.6	—	0.939	(9, 22)

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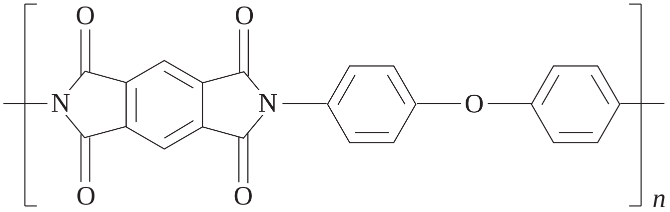
Poly(pyromellitimide-1,4-diphenyl ether)

LOON-SENG TAN

ACRONYMS, TRADE NAMES ODA-PMDA, PMDA-ODA, Kapton®, Vespel®, Apical®

CLASS Polyimides; high-performance polymers

STRUCTURE



SYNTHESIS Poly(pyromellitimide-1,4-diphenyl ether) is generally prepared from polycondensation of pyromellitic dianhydride and 4,4′-oxydianiline followed by either thermal or chemical (in the presence of acetic anhydride and triethylamine) cyclodehydration of the polyamic acid precursor.

MAJOR APPLICATIONS Kapton films are used as wire and cable wrap, formed coil wrap, motor-slot liners, substrates for flexible printed circuit boards, magnetic-wire insulation, and in transformers and capacitors.[1] Vespel molded parts are used in automobiles, large on-and-off-road vehicles, farm equipment, business machines, electronic equipment, etc.: rotary seal rings, thrust washers and discs, bushings, flanges bearings, printer platen bars, plungers, printer wireguides, stripper fingers, spline couplings, wear strips, locknut inserts, valve seats, check valve balls, thermal and electrical insulators.[2]

PROPERTIES OF SPECIAL INTEREST Kapton films have excellent thermal stability in air or inert atmosphere, useful mechanical properties over very broad temperature range, outstanding electrical properties and stability of these electrical properties over wide range of relative humidity, insensitive to solvents, excellent radiation resistance; considerable variation in hydrolytic sensitivity, poor hydrolytic resistance in 10% NaOH.[3] Vespel direct-formed parts are resistant to thermally harsh environment, creep, impact, and wear, and friction at high pressures and velocities.[4]

PRODUCT NAMES	PRODUCT DESCRIPTIONS	SUPPLIER
Kapton	Polyimide films available in three types: 1. HN film 2. VN films 3. FN films Both HN and VN films are all-polyimide films, but FN films are coated on one or both sides with Teflon FEP fluoropolymer resin	DuPont High Performance Films, U.S. Route 23 and DuPont Road, P.O. Box 89, Circleville, Ohio 43113, USA DuPont de Nemours (Luxembourg S.A.) Contern, L-2984 Luxembourg, Grand Duchy of Luxembourg DuPont Kabushi Kaisha, Arco Tower, 8-1, Shimomeguro 1-chrome, Meguro-ku, Tokyo 153, Japan

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PRODUCT NAMES	PRODUCT DESCRIPTIONS	SUPPLIER
Vespel	Available in 5 compositions: 1. SP-1, unfilled based resin 2. SP-21, 15% by wt. graphite filler 3. SP-22, 40% by wt. graphite filler 4. SP-211, 15% by wt. graphite and 10% by wt. Teflon fluorocarbon resin fillers 5. SP-3, 15% by wt. molybdenum disulfide (for lubrication)	Du Pont Engineering Polymers, Pencader Site, Newark, Delaware 19714-6100, USA Du Pont de Nemours (Belgium) N. V., Du Pont Engineering Polymers, Antoon Spinoystraat 6, B-2800 Mechelen, Belgium Du Pont Japan Limited, Specialty Polymers, VESPEL, Marketing, 19-2, Kiyohara, Kogyo Danchi, Utsunomiya, Tochigi, 321-32, Japan
Apical	Polyimide films	Kanegafuchi Chemical Industry Company Ltd., Japan

Mechanical properties of Kapton HN film (25 μm)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Ultimate tensile strength	MPa	ASTM D-882		(1, 5)
		Method A; film size, 25 × 150 mm; 23°C	231	
		200°C	139	
Yield point at 3%	MPa	ASTM D-882		(1, 5)
		23°C	69	
		200°C	41	
Stress to produce 5% elongation	MPa	ASTM D-882,		(1, 5)
		23°C	90	
		200°C	61	
Ultimate elongation	%	ASTM D-882		(5)
		−195°C	2	
		23°C	72	(1, 5)
		200°C	83	(1, 5)
Tensile modulus	MPa	ASTM D-882		
		−195°C	3,500	(5)
		23°C	2,500	(1, 5)
		200°C	2,000	(1, 5)
Folding endurance (MIT)	cycles	ASTM D-2176; 23°C	285,000	(1, 5)
Tear strength-propagating (Elmendorf)	N	ASTM D-1922; 23°C	0.07	(1, 5)
Tear strength-initial (Graves)	N	ASTM D-1004; 23°C	7.2	(1, 5)
Poisson's ratio	–	Average of 3 samples elongated at 5%, 7%, and 10%	0.34	(1, 5)

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Poly(pyromellitimide-1,4-diphenyl ether)

Thermal properties of Kapton HN film (25 μm)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melting point	K	ASTM E-794	–	(1, 5)
Thermal coefficient of linear expansion	10^{-6} K^{-1}	ASTM D-696; −14 to 38°C	20	(1, 5)
Coefficient of thermal conductivity	$W m^{-1} K^{-1}$	ASTM F-433, 296 K	0.12	(1)
Specific heat	$J g^{-1} K^{-1}$	Differential calorimetry	1.09	(1)
Flammability	–	UL-94	94V-0	(1)
Shrinkage	%	IPC TM 650, method 2,2.4A; 30 min at 150°C	0.17	(1)
		IPC TM 650, method 2,2.4A; 30 min at 250°C	0.3	(5)
		ASTM D-5214; 120 min at 400°C	1.25	(1)
Smoke generation	–	NFPA-258; NBS smoke chamber	DM ≤ 1	(1)
Glass transition temperature	K	–	633–683	(1)
Cut-through temperature	K	25 μm thickness; at 25°C	708	(1, 5)
		50–125 μm thickness; at 25°C	798	(1, 5)

Optical properties of Kapton film (25 μm)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Refractive index	–	Visible range	1.70–1.80	(6, 7)

Electrical properties of Kapton HN film (25 μm)

PROPERTIES	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric strength	$V \mu m^{-1}$	ASTM D-149; 23°C, 50% RH, 60 Hz, 1/4 in electrodes, 500 $V s^{-1}$ rise	303	(1, 5)
Dielectric constant	–	ASTM D-150; 23°C, 50% RH, 10^3 Hz, 23°C, 50% RH	3.4	(1, 5)
		ASTM D-150; 23°C, 50% RH 10^3 Hz, 200°C, 50% RH	3.0	(1, 5)
Dissipation factor	–	ASTM D-150		(1, 5)
		23°C, 50% RH, 10^3 Hz, 23°C, 50% RH	0.003	
		23°C, 50% RH, 10^3 Hz, 200°C, 50% RH	0.002	

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PROPERTIES	UNITS	CONDITIONS	VALUE	REFERENCE
Volume resistivity	ohm cm	ASTM D-257; 23°C, 50% RH ASTM D-150; 200°C, 50% RH	10^{18} 10^{14}	(1, 5)
Corona start voltage	volts	At 50% RH, 25°C	465	(1, 5)
Surface resistivity	ohm	25°C	10^{16}	(1, 5)
Loss tangent: $\tan\delta$	–	60 Hz 1 KHz 1 MHz	0.003 0.0025 0.011	(7)
Dielectric breakdown voltage (D.C.)	$V\,cm^{-1}$	– 60 Hz	1.2×10^5 2.76×10^6	(7)

Permeability of Kapton film (25 μm)[1,5]

Gas	Units	Conditions	Value
He	$ml\,m^{-2}\,day^{-1}\,MPa^{-1}$	ASTM D-1434-82; 23°C, 50% RH	63,080
CO_2	$ml\,m^{-2}\,day^{-1}\,MPa^{-1}$	ASTM D-1434-82; 23°C, 50% RH	6,840
H_2	$ml\,m^{-2}\,day^{-1}\,MPa^{-1}$	ASTM D-1434-82; 23°C, 50% RH	38,000
N_2	$ml\,m^{-2}\,day^{-1}\,MPa^{-1}$	ASTM D-1434-82; 23°C, 50% RH	910
O_2	$ml\,m^{-2}\,day^{-1}\,MPa^{-1}$	ASTM D-1434-82; 23°C, 50% RH	3,800
Vapor			
H_2O	$g\,m^{-2}\,day^{-1}\,MPa^{-1}$	ASTM E-96-92; 23°C	54

Other physical properties of Kapton film (25 μm)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Limiting oxygen Index	%	ASTM D-2863-87	37	(1, 5)
Surface tension	$mN\,m^{-1}$	20°C	37.7	(8)
Hygroscopic coefficient of expansion	ppm $(\%RH)^{-1}$	23°F, 20–80% RH	22	(1, 5)
Moisture absorption	%	50% RH, 23°C Immersion 24 h at 23°C	1.8 2.8	(1, 5)
Density	$g\,cm^{-3}$	ASTM D-1505-90	1.42	(1)
Coefficient of friction	–	Kinetic (film-to-film)	0.48	(1)
Coefficient of friction	–	Static (film-to-film)	0.63	(1)

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Mechanical properties of Vespel (SP-1 polyimide resin)

PROPERTIES	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength, ultimate	MPa	ASTM-D 1708		(4, 9)
		23°C	86.2	
		260°C	41.4	
Elongation, ultimate	%	ASTM-D 1708		(4, 9)
		23°C	7.5	
		260°C	6.0	
Flexural strength, ultimate	MPa	ASTM-D 790		(4, 9)
		23°C	110.3	
		260°C	62.1	
Flexural modulus	MPa	ASTM-D 790		
		23°C	3,102	(4, 9)
		260°C	1,724	(4)
Compressive stress	MPa	ASTM-D 695		(4)
		23°C, at 1% strain	24.8	
		23°C, at 10% strain	133.1	
		23°C, at 0.1% offset	51.0	
Compressive modulus	MPa	ASTM-D 695; 23°C,	2413	(4)
Axial fatigue endurance limit	MPa	At 10^3 cycles and 23°C	55.8	(4)
		At 10^3 cycles and 260°C	42.1	(4, 9)
		At 10^3 cycles and 23°C	55.8	(4, 9)
		At 10^7 cycles and 260°C	16.5	(4, 9)
Flexural fatigue endurance limit	MPa	At 10^3 cycles and 23°C	65.5	(4, 9)
		At 10^7 cycles and 23°C	44.8	
Shear strength	MPa	ASTM-D 732; 23°C	89.6	(4, 9)
Impact strength, notched Izod	$J m^{-1}$	ASTM-D 256; 23°C	42.7	(4, 9)
Impact strength, unnotched Izod	$J m^{-1}$	ASTM-D 256; 23°C	747	(4, 9)
Poisson's ratio	–	23°C	0.41	(4, 9)

Wear and friction properties of Vespel (SP-1 polyimide resin)

PROPERTIES	UNITS	CONDITIONS	VALUE	REFERENCE
Friction coefficient	–	Steady state, unlubricated in air ($PV = 0.875\, MPa\, m\, s^{-1}$)	0.29	(4, 9)
		Static in air	0.35	
Wear rate	$cm\ (1{,}000\, h)^{-1}$	Unlubricated in air	0.64–3.0	(9)

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Thermal properties of Vespel (SP-1 polyimide resin)

PROPERTIES	UNITS	CONDITIONS	VALUE	REFERENCE
Coefficient of linear expansion	10^{-6} K^{-1}	ASTM-D 696		(4, 9)
		23–300°C (m/m)	54	
		−62 to 23°C	45	
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	40°C	0.35	(4, 9)
Specific heat	$J\,Kg^{-1}\,K^{-1}$	–	1,130	(4)
Deformation	%	ASTM-D 621; under 2,000 psi load	0.14	(4, 9)
Deflection temperature	K	ASTM-D 648; at 264 psi	~633	(4, 9)

Electrical properties of Vespel (SP-1 polyimide resin)[4, 9]

PROPERTIES	UNITS	CONDITIONS	VALUE
Dielectric constant	–	ASTM-D 150	
		At 10^2 Hz, 23°C	3.62
		At 10^4 Hz, 23°C	3.64
		At 10^6 Hz, 23°C	3.55
Dissipation factor	–	ASTM-D 150	
		10^2 Hz, 23°C	0.0018
		10^4 Hz, 23°C	0.0036
		10^6 Hz, 23°C	0.0034
Dielectric strength	$MV\,m^{-1}$	ASTM-D 149; short time, 0.002 m thick	22
Volume resistivity	ohm m	ASTM-D 257; 23°C	10^{14}–10^{-15}
Surface resistivity	ohm	ASTM-D 257; 23°C	10^{15}–10^{-16}

Other physical properties of Vespel (SP-1 polyimide resin)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Water absorption	%	ASTM-D 570; 24 h at 23°C	0.24	(4, 9)
		Immersion 48 h at 50°C	0.72	
Equilibrium	–	50% RH	1.0–1.3	(4, 9)
Specific gravity	–	ASTM-D 792	1.43	(4, 9)
Hardness	Rockwell E	ASTM-D 785	45–60	(4, 9)
	Rockwell M	ASTM-D 785	92–102	(9)
Limiting oxygen index	%	ASTM-D 2863	53	(4, 9)

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Poly(pyromellitimide-1,4-diphenyl ether)

Fiber properties of poly(pyromellitimide-1,4-diphenyl ether)* [(10)]

PROPERTIES	UNITS	CONDITIONS	VALUE
Tenacity	MPa ($\times 10^3$)	Heat treated under tension at 525–575°C	0.45–0.72
Elongation	%	Heat treated under tension at 525–575°C	9.0–11.7
Modulus	MPa ($\times 10^3$)	Heat treated under tension at 525–575°C	6.4–9.9

*Fibers were spun from poly(amic acid)/dimethylacetamide solutions and the resultant poly(amic acid) fibers were then thermally converted to polyimide fibers under sufficient tension. The polyimide fiber was finally heat treated at 525–575°C.

Transition temperatures of poly(pyromellitimide-1,4-diphenyl ether)

Test Method/Conditions	T_g (K)	T_m (K)	Reference
DSC, 20°C/min; film sample	693	—	(11)
DSC; film thickness ~ 12.5 mm	683	—	(12)
DSC; film sample	673	—	(13)
Thermomechanical technique	650		(14)
Thermomechanical technique; film thickness ~ 20 mm	—	870	(14, 15)

Secondary-relaxation temperatures of poly(pyromellitimide-1,4-diphenyl ether)

Test Method/Conditions	T_β (K)	E_a (kJ mol^{-1})	T_γ (K)	E_a (kJ mol^{-1})	Reference
Resonance electrostatic method; 15,000 Hz	400	84–105	250	66	(17)
Resonance electrostatic method; 14,000 Hz	405	—	—	—	(18)
Torsion pendulum; 1 Hz	—	—	185	317	(19)

*Adapted from reference (16).

Unit cell dimensions

Lattice	Monomer	Cell dimension (Å)			Cell angles (degrees)			Reference
	per unit cell	*a*	*b*	*c* (chain axis)	α	β	γ	
Orthorhombic	2	6.35	4.05	32.6	90	90	90	(20)
Orthorhombic	2	6.31	3.97	32	90	90	90	(21)
Monoclinic	2	4.66	32.9	5.96 15.9	90	100	90	(22)

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Structural parameters of poly(pyromellitimide-1,4-diphenyl ether)

PROPERTY	UNIT	CONDITIONS	VALUE	REFERENCE
Repeat distance	Å	X-ray diffraction	16	(21)
Mean interchain d-spacing	Å	X-ray diffraction	4.45	(13)
Persistent length	Å	Theoretical calculation	36	(23)
Kuhn segment	Å	Theoretical calculation	72	(23)

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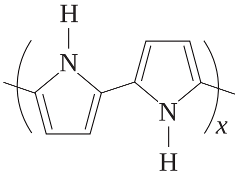
Polypyrrole

SHRISH RANE AND GREG BEAUCAGE

ACRONYM PPy

CLASS Polyheterocyclics; conjugated conducting polymers

STRUCTURE The pyrrole rings are mainly linked in the α, α' positions giving a planar geometry. There is evidence of other bonding observed through NMR and IR analysis.[1,2,3]



MAJOR APPLICATIONS At present there are no commercial applications for polypyrrole. It does show potential for use in display devices, chemical sensors, electrodes in batteries, drug carriers, heating fabrics, deionizers, and as a catalyst.

PROPERTIES OF SPECIAL INTEREST Presence of an extended π-bonding system, which imparts electrical properties to the polymer. Doping either *p* or *n* can enhance these properties. Polypyrrole is stable in air at room temperature as well as at temperatures as high as 250°C in its doped state. Also, polypyrrole can be synthesized in a doped state. It changes color when switched from its conducting to insulating state.

PROPERTY	UNITS	CONDITIONS	VALUES	REFERENCE
Chemical synthesis	Oxidative polymerization in either solution or vapor phase Polymerization on colloidal cerium oxide particles In the presence of ammonium persulfate (oxidant) and dodecylbenzene sulfonic acid (dopant)			(2, 4)
Electrochemical synthesis	Electrodes: anode (platinum, *n*-type silicon, conducting glass, stainless steel, gold/glassy Carlson); cathode (copper) Electrolytes: copper sulfate, acetonitrile + *p*-toluenesulfonoc acid (HTSO), lithium perchlorate, sodium perchlorate, sulfuric acid			(1, 5–7)
Conductivity σ	S cm^{-1}	Measured Orienting the film by mechanical methods improves the measured value	100 ~1,000	(1, 8)
Optical properties	PPy films coated on electrodes undergo a color change when they switch from an oxidized to a reduced state and vice–versa			(1, 9, 10)

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PROPERTY	UNITS	CONDITIONS	VALUES	REFERENCE
Solubility		Neutral PPy is by and large insoluble In its doped state it is soluble in chloroform, DMSO, *m*-cresol, and NMP		(1, 11)
Thermal stability	K	In air	523	(1)
UV-Vis spectroscopy	nm	Strong absorption band in doped state on a platinum electrode	272	(1, 12, 13)
		Neighboring shoulder peaks	368 and 381	

Polymer	Peak (eV)
Oxidised PPy	1.0
-do-	3.0
Neutral PPy	1.3
-do-	3.2

^{13}C NMR[14]

Polymer	Shift from TMS (ppm)	Conditions
Neutral PPy	~123	α carbon
	~105	β carbon
	~135	Non-α-α' linkages or chain end groups

PROPERTY	UNITS	CONDITIONS	VALUES	REFERENCE
IR properties	cm^{-1}	PPy electropolymerized under oxygen free conditions		(1, 13, 15)
		O–H stretch	2,930–2,800	
		C–O stretch	1,750–1,650	
		C–O–C asymmetrical stretch	1,099	
		Electropolymerized PPy-perchlorate first electropolymerized and then reduced to its neutral state		
		Neutral Ppy		
		NH band	3,400	
		CH band	3,100	
		C–H stretching	2,870–2,960	
		Pyrrole bands	<1,800	
		Ppy-perchlorate		
		NH band	Absent*	
		CH band	Absent	
		C–H stretching	–	
		Pyrrole bands	<1,800	

*Masked by the tail of the 1-eV peak.

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Polypyrrole

Crystallinity*[2]

Lattice	Unit cell dimensions (nm)			Cell angles (degrees)		
	a	*b*	*c*	α	β	γ
Monoclinic	0.82	0.735	0.682	90	90	117

*PPy shows very low crystallinity.

PROPERTY	UNITS	CONDITIONS	VALUES	REFERENCE
Density	$g\ cm^{-3}$	–	1.47	(2)
Molecular weight	It is difficult to measure the molecular weight of PPy because it is insoluble. Indirect methods on substituted PPs has yielded the number of molecular units as being between 100 and 1,000, contingent upon the polymerization method.			(1, 3)
Morphology	SEM studies on electropolymerized PPy show globular particle aggregates. The surface morphology is influenced by the electrolyte used. Its appearance ranges from a rough dendritic surface in CH_3CN to a smoother surface in low amounts of water and other hydroxylic solvents. STM images of p-toluenesulfonate doped PPy show small islands interconnected by 1.5–2 nm wide fibrils.			(1, 13, 14, 16)

Mechanical properties of PPy-toluenesulfonate films*[17,18]

Electrolyte	Elongation at break (%)	Young's modulus (MPA)	Applied voltage (V)
$NaNO_3$	4–10	$2,386 \sim 1,930$	+0.4 to −0.8
$Mg(NO_3)_2$	3–8	$2,014 \sim 2,176$	+0.4 to −0.8
KCL	5–14	$3,415 \sim 1,415$	0 to −0.5
LiCL	7–21	$3,666 \sim 2,650$	0 to −0.5
NaCL	5–21	$3,621 \sim 2,193$	0 to −0.5
$MgCL_2$	6–7	$2,611 \sim 3,609$	0 to −0.5
H_2O	9	2,914	0 to −0.5

*Samples: 30 mm long, 5 mm wide, dumb-bell shaped.

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Cosolvent	Ratio	Young's modulus (Pa)	Elongation at break (%)
H_2O-ACN	1:99	2,413.2	4
-do-	1:99	827.4	17
-do-	25:75	482.6	4
EG-ACN	25:75	1,103.2	5
-do-	50-50	896.3	8
H_2O-EG-CAN	1:1:98	1,379	8
-do-	2:5:93	1,034.2	8
-do-	5:5:90	896.3	14
-do-	12.5:12.5:75	827.4	7
-do-	25:25:50	1,034.2	6
H_2O-EG	50:50	344.7	6
G-ACN	1:99	1,310	8
G-H_2O	50:50	1,654.7	6

*15–35 μm thick in various ACN-Co-solvent systems.

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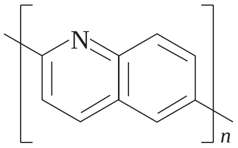
Polyquinoline

SHRISH RANE AND GREG BEAUCAGE

ACRONYM PQ

CLASS Polyheterocyclics; polyaromatics

STRUCTURE The structure of PQ can vary from a semirigid to a rigid-rod one depending on the synthesis conditions.



MAJOR APPLICATIONS Polyquinolines can be processed into films and fibers and can be spin coated. An ideal choice for high-performance films, electronic coatings, as a matrix for high-performance composites, and as an interlayer dielectric substrate in multichip modules.

PROPERTIES OF SPECIAL INTEREST The structure of polyquinolines can be altered from a semirigid chain to a rigid one during the synthesis. Although largely an amorphous polymer, some substituted rigid-rod members exhibit crystallinity in low amounts. Polyquinolines are found to posses excellent thermal and oxidative stability, good mechanical properties, low dielectric constants, low values of moisture absorption, and low thermal expansion coefficients.

SYNTHESIS[1–4]

(a) Acid or base catalyzed Friedlander synthesis.
(b) Catalytic dehydrogenative polycondensation of nonsubstituted quinoline oligomers from 1,2,3,4,-tetrahydroquinoline in the presence of transition metal catalysts.
(c) Condensation reaction of 3,3′-dibenzoylbenzidine with diacetyl and diphenyl compounds.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Ionization potential	eV	Calculated on PQ using the Valence Effective Hamiltonian Technique (VEH)		(5–8)
		Gas phase	7.89	
		Solid phase	~6.0	
Dielectric constant	–	Range; measured on 28 μm PQ100 (thermoplastic PQ) film	2.5–2.6	(5–8)
Band-gap	eV	Calculated on PQ using the Valence Effective Hamiltonian Technique (VEH)	3.2	(5–8)
Electrooptic coefficient (r_{33}) wavelength	mm	Measured on a 20% wt. RT-9800/PQ film poled at 0.8 MV cm^{-1}	1.3	(7)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Conductivity	$S\,cm^{-1}$	Vapor phase thermolysed PQ film CVD deposited PQ film	400 695 ~ 920	(1, 2, 9)
Thermal stability	TGA wt. loss	Air N_2	500–600 ~800	(1, 4, 10, 11)
Glass transition temperature T_g	K	–	523–663	(1, 4, 10, 11)
Crystallization temperature T_c	K	In case for the rigid-rod varieties of polyquinoline	688–703	(1, 4, 10, 11)
Melting temperature T_m	K	In case for the rigid-rod varieties of polyquinoline	721–823	(1, 4, 10, 11)
Solubility	The solubility of PQ is dependent upon its molecular architecture. Generally it is soluble in a variety of organic solvents (e.g., $CHCl_3$, *m*-cresol, THF, H_2SO_4, and TCE).			(1, 7, 12)
Tensile strength	MPa	–	97	(1, 4, 11)
Tensile modulus	MPa	–	2,680	(1, 4, 11)
Elongation at break	%	–	6.2	(1, 4, 11)
Young's modulus	MPa	Rigid-rod PQ Semirigid PQ	4,800 1,900	(1, 4, 11)
Morphology	SEM studies on PQ films show a smooth surface with dense domains without any distinguishing characteristics like fibrils or filaments. TEM on the semirigid PQs reveal an amorphous structureless regime without any ordered structure.			(9)
Crystallinity	%	–	20–65	(1, 3, 4)
PQ fiber crystalline *d* spacings	Å	–	10.23, 10.30, 10.31	(4)

Solution properties*(13)

Properties/Parameters	η (ml g^{-1})†	k'†	M_w (g mol^{-1})‡	$R_g^2 \times 10^{10}$ (cm^2)‡	$A_2 \times 10^4$ (ml mol g^{-1})‡	M_e (g mol^{-1})‡
Values	28 ~ 61	0.38 ~ 0.72	17,000 ~ 60,000	0.2 ~ 0.19	3 ~ 18	23,000 ~ 110,000

*Solvents used were *m*-cresol, chloroform, and THF.
†From intrinsic viscosity measurements.
‡From light scattering measurements. For a complete description of the samples, see reference (2).

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Poly(rotaxane), example 1

AKIRA HARADA

ACRONYMS, ALTERNATIVE NAME PR, MN, molecular necklace

CLASS Cyclic polymers

STRUCTURE $(NO_2)_2{-}C_6H_3{-}NH{-}(CH_2CH_2O)_n{-}CH_2CH_2NH{-}C_6H_3{-}(NO_2)_2 + m(C_6H_{10}O_5)_6$

MAJOR APPLICATIONS Starting materials for tubular polymers. Potential use for curing of PEG.

PROPERTIES OF SPECIAL INTEREST Stable under ambient conditions. Relatively low cost.

PROPERTY	UNITS	CONDITIONS	VALUES	REFERENCE
Decomposing point	K	MN-1450	593	(1)
		MN-2000	593	(1)
		MN-3350	603	(2)
Molecular weight	$g\ mol^{-1}$	MN-1450	16,500	(1)
		MN-2000	20,000	(1)
		MN-3350	23,500	(2)
		MN-1248	13,244	(3)
		MN-8500	44,000	(4)
Molecular weight (of repeat unit)	$g\ mol^{-1}$	MN-1450	1,375	(1)
		MN-2000	1,111	(1)
		MN-3350	1,175	(2)
		MN-1248	1,060	(3)
Number of cyclodextrins	—	MN-1450	15	(1)
		MN-2000	18	(1)
		MN-3350	23	(2)
		MN-1248	12	(3)
		MN-8500	36	(4)
IR (characteristic absorption frequencies)	cm^{-1}	MN-1450	3,386	(1)
			2,923	
			1,153	
			1,077	
			1,029	
UV (characteristic absorption frequencies)	nm	MN-1450	360	(1)
	ε, $l\ mol^{-1}\ cm^{-1}$		17,950	

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Poly(rotaxane), example 1

PROPERTY	UNITS	CONDITIONS	VALUES	REFERENCE
^{1}H-NMR	ppm	MN-1450, (DMSO-*d6*), 270 MHz		(1)
		Phenyl	7.27–8.88	
		Cyclo-dextrin	3.2–5.45	
		PEG	3.52	
^{13}C-NMR	ppm	MN-1450, (DMSO-*d6*), 125.65 MHz		(1)
		Cyclo-dextrin	71.46–101.90	
		PEG	69.35	
Specific rotation	degrees unit^{-1}	MN-1450, DMSO, 25°C, 589 nm	160	(1)
Solvent	DMSO			(1)
	0.1N NaOH			(5)
Nonsolvent	Organic solvent (benzene, hexane, acetone, chloroform), H_2O			(1)
Water content	w/w%	–	>10	–

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Poly(rotaxane), example 2

AKIRA HARADA

ACRONYM, ALTERNATIVE NAME PR, molecular bracelet

CLASS Cyclic polymers

STRUCTURE*
$(RC_6H_4)_3{-}CH_2CH_2O(CO{-}(CH_2)_m{-}CO{-}O{-}(CH_2CH_2O)_nCH_2CH_2O)_x{-}$
$CO{-}(CH_2)_8{-}CO{-}O{-}(R{-}C_6H_4)_3$ + 30-crown-10[$(CH_2CH_2O)_{10}$], or
42-crown-14[$(CH_2CH_2O)_{14}$], or 60-crown-20 [$(CH_2CH_2O)_{20}$]

MAJOR APPLICATIONS Potential use for curing of polyesters.

PROPERTIES OF SPECIAL INTEREST Stable under ambient conditions. Soluble in organic solvents.

PROPERTY	UNITS	CONDITIONS*	VALUES	REFERENCE
Molecular weight	$g\,mol^{-1}$	8,10,3-crown-10	4,000	(1)
		8,4,3-crown-10	8,700	
		8,2,3-crown-10	12,200	
		8,2,3-crown-10	24,000	
m/n	–	8,10,3-crown-10	0.15	(1)
		8,4,3-crown-10	0.028	
		8,2,3-crown-10	0.24	
		8,2,3-crown-10	0.31	
Molecular weight (of repeat unit)	$g\,mol^{-1}$	8,10,3-crown-10	$440m + 307n$	(2)
		8,4,3-crown-10	$440m + 168n$	
		8,2,3-crown-10	$440m + 268n$	
$[\eta]$	$dl\,g^{-1}$	8,2,3-crown-10	0.28	(1)
Mass % cyclic	–	8,10,3-crown-10	16	(1)
		8,4,3-crown-10	5.5	
		8,2,3-crown-10	24	
		8,2,3-crown-10	30	
Melting temperature T_m	K	8,2,3-crown-10	278, 291	(1)
		8,2,3-crown-10	282, 286	
T_c	K	8,2,3-crown-10	264	(1)
		8,2,3-crown-10	265	
Glass transition temperature T_g	K	8,2,3-crown-10	219	(1)
		8,2,3-crown-10	217.3	
Solvents	–	8,2,3-crown-10	Acetone, THF, CH_2Cl_2	(1)

*m,n,3-crown-10.

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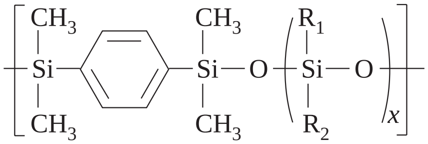
Poly(silphenylene-siloxanes)

MICHAEL J. OWEN AND PETAR R. DVORNIC

ALTERNATIVE NAMES, TRADE NAMES Silphenylenes, silarylene-siloxane polymers

CLASS In-chain modified polysiloxanes

STRUCTURE



MAJOR APPLICATIONS Precursors for elastomers having increased thermal and thermo-oxidative stability while retaining low glass transition temperatures (i.e., gaskets, sealants, O-rings). Established method of building chain stiffness into polysiloxanes. Gas semipermeable membranes with increased separation ability retained high permeability (relative to polysiloxanes). Have been used as laminate impregnating resins in electrical insulation applications where heat resistance is required.

PROPERTIES OF SPECIAL INTEREST Partial replacement of siloxane units in polysiloxanes with silphenylene groups increases polymer chain stiffness, glass transition temperature, viscosity, crystallinity, thermal, thermo-oxidative, and solvent resistance. Many mechanical properties also improved although low-temperature elasticity is somewhat diminished. The best combination of properties is obtained for $x = 1$ in the above structure (the so-called "exactly alternating silphenylene-siloxane polymers") although derivatives with $x = 0$ through $x = 4$ are also known. Many different homologues with various siloxanylene side groups (R_1 and R_2 in the formula above) have been reported, as well as meta-silphenylenes, although a good method for the synthesis of meta-phenylene containing monomer(s) has not been developed as yet.

Preparative techniques

Type of polymerization	Conditions	Polymer molecular weight ($g\,mol^{-1}$)	Typical polydispersity index ($\overline{M}_w/\overline{M}_n$)	References
(a) Self condensation of phenylenedisilanols	In melt or in refluxing solvent. Catalysts: NaOH; KOH; LiOH; K_2O. Solvents: benzene, toluene.	1,000–100,000	2–6	(1, 2, 3)
(b) Solution polycondensation of phenylenedisilanols and dichlorosilanes	In nitrogen. Solvents: THF, toluene or chlorobenzene. Room temperature or below.	30,000–50,000	1,6–2,2	(1, 4, 5, 6)
(c) Solution polycondensation of phenylenedisilanes and diaminosilanes	In nitrogen. Solvents: refluxing toluene or benzene.	50,000–500,000	1,8–2,2	(1, 4, 7–9, 22)

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Type of polymerization	Conditions	Polymer molecular weight (g mol^{-1})	Typical polydispersity index ($\overline{M}_w/\overline{M}_n$)	References
(d) Solution polycondensation of phenylenedisilanols and diacetoxysilanes	In nitrogen. Solvents: refluxing toluene. Catalysts: triethylamine; *n*-hexylamine; 2,4,6-trimethylpyridine.	30,000–80,000	1,8–2,2	(1, 4, 10)
(e) Solution polycondensation of phenylenedisilanols and *bis*ureidosilanes	In nitrogen. Solvent: chlorobenzene. Temperature: −20°C to room temperature	100,000–800,000	1,8–2,2	(1, 4, 11)
Typical comonomers	*P*-phenylenedisilanols (a–e) + dichlorosilanes (b); diamino-silanes (c); diacetoxysilanes (d); bisureidosilanes (e)			—

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	g mol^{-1}	$x = 1$ and $R_1 = R_2 = CH_3$	283	—
Typical molecular weight range of polymer ($\overline{M}_w$)	g mol^{-1}	For most preparative procedures (a–e) (see above table)	30,000–150,000	—
Typical polydispersity index ($\overline{M}_w/\overline{M}_n$)	—	—	1.8–2.3	—
Density	g cm^{-3}	$x = 0$; $R_1 = R_2 = CH_3$; room temperature	1.102 1.103	(19) (3)
Unit cell dimensions	Å	$x = 0$; $R_1 = R_2 = CH_3$; tetragonal	$a = 9.08$, $b = 9.08$, $c = 15.38$ $a = 9.02$, $b = 9.02$, $c = 15.43$	(19) (21)
Unit cell contents	—	$x = 0$; $R_1 = R_2 = CH_3$; tetragonal	4 4	(19) (21)
Heat of fusion (of repeat unit)	kJ mol^{-1}	$x = 0$; $R_1 = R_2 = CH_3$; depression of T_m in mixtures	18.2	(3)
Solvents	—	—	THF, toluene, chlorobenzene	(1)
Nonsolvents	—	—	Methanol	(1)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Mark-Houwink parameters: K and a	$K = \text{ml g}^{-1}$ a = None	$x = 0$; $R_1 = R_2 = CH_3$; toluene/25°C; $\overline{M}_w$ = 70,000–400,000	$K = 1.12 \times 10^{-4}$, $a = 0.75$	(3)
		$x = 1$; $R_1 = R_2 = CH_3$; THF/30°C, $\overline{M}_w$ = 30,000–109,000	$K = 7.86 \times 10^{-5}$, $a = 0.757$	(9)
		$x = 1$; $R_1 = CH_3$; $R_1 = C_6H_5$; THF/30°C, $\overline{M}_w$ = 38,000–245,000	$K = 5.34 \times 10^{-5}$, $a = 0.749$	(9)
		$x = 1$; $R_1 = R_2 = C_6H_5$; THF/30°C, $\overline{M}_w$ = 76,000–240,000	$K = 3.28 \times 10^{-5}$, $a = 0.821$	(9)
Glass transition temperature	K	$x = 0$		
		TBA	248	(9, 12)
		Dlatometry	256	(13)
		$x = 1$; $R_1 = R_2 = CH_3$		
		TBA	212	(9)
		DSC (20° min^{-1})	211	(12, 14)
		DSC (5° min^{-1})	209	(12, 14)
		$x = 2$; $R_1 = R_2 = CH_3$		
		DTA	210	(7)
		TBA	185	(9)
		$x = 3$; $R_1 = R_2 = CH_3$		
		DTA	201	(7)
		TBA	171	(9)
		$x = 4$; $R_1 = R_2 = CH_3$		
		DTA	193	(7)
		TBA	164	(9)
		$x = 1$; $R_1 = CH_3$; $R_1 = C_6H_5$		
		TBA	248	(9)
		DSC	241	(9)
		$x = 1$; $R_1 = CH_3$; $R_1 = (CH_2)_2CN$; DSC	236	(12, 16)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH_2)_3CN$; DSC	236	(12, 16)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH_2)_2CF_3$; DSC	222	(12, 15)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH_2)_2(CF_2)_5CF_2$; DSC	218	(12, 15)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH_2)_2CH_3$; DSC	208	(12, 16)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH_2CH{=}CH_2)$; DSC	207	(12, 16)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH{=}CH_2)$; DSC	204 198	(12, 14) (12, 14)
		$x = 1$; $R_1 = R_2 = C_6H_5$		
		TBA	274	(9)
		DSC	269	(9)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature	K	$x = 1$; $R_1 = C_6H_5$; $R_2 = (CH{=}CH_2)$; DSC	242	(12)
		$x = 1$; $R_1 = C_6H_5$; $R_2 = (CH_2CH{=}CH_2)$; DSC	235	(12)
		$x = 1$; $R_1 = R_2 = (CH_2)_3CN$; DSC	243	(12, 16)
		$x = 1$; $R_1 = H$; $R_2 = (CH_2)_2CF_3$; DSC	236	(12, 15)
Melting point	K	$x = 0$; $R_1 = R_2 = CH_3$	421	(3)
			425	(19)
Thermal stability in nitrogen*	K	$x = 1$; $R_1 = R_2 = CH_3$; TGA ($10^\circ\ min^{-1}$)	673	(1, 17)
		$x = 1$; $R_1 = H$; $R_2 = CH_3$; TGA ($10^\circ\ min^{-1}$)	463	(1)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH_2)_2(CF_2)_5CF_3$; TGA ($10^\circ\ min^{-1}$)	423	(1, 18)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH{=}CH_2)$		
		TGA ($10^\circ\ min^{-1}$)	753	(1, 17)
		TGA ($15^\circ\ min^{-1}$)	820	(22)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH_2)_2CH_3$; TGA ($15^\circ\ min^{-1}$)	818	(1, 16)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH_2CH{=}CH_2)$; TGA ($15^\circ\ min^{-1}$)	778	(1, 16)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH_2)_2CN$; TGA ($15^\circ\ min^{-1}$)	768	(1, 16)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH_2)_3CN$; TGA ($15^\circ\ min^{-1}$)	798	(1, 16)
		$x = 1$; $R_1 = CH_3$; $R_2 = C_6H_5$; TGA ($15^\circ\ min^{-1}$)	668	(22)
		$x = 1$; $R_1 = R_2 = (CH_2)_3CN$; TGA ($15^\circ\ min^{-1}$)	783	(1, 16)
		$x = 1$; $R_1 = C_6H_5$; $R_2 = (CH_2CH{=}CH_2)$; TGA ($15^\circ\ min^{-1}$)	807	(1, 16)
Thermo-oxidative stability in air*	K	$x = 1$; $R_1 = R_2 = CH_3$; TGA ($10^\circ\ min^{-1}$)	618	(1, 17)
		$x = 1$; $R_1 = H$; $R_2 = CH_3$; TGA ($10^\circ\ min^{-1}$)	453	(1)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH_2)_2(CF_2)_5CF_3$	423	(1, 18)
		$x = 1$; $R_1 = CH_3$; $R_2 = (CH{=}CH_2)$; TGA ($15^\circ\ min^{-1}$)	704	(22)
		$x = 1$; $R_1 = CH_3$; $R_1 = C_6H_5$; TGA ($15^\circ\ min^{-1}$)	669	(22)
Tensile modules	MPa	$x = 1$; $R_1 = R_2 = CH_3$; 20–30% wt. silica filler; <3% cross-linking agent; <3 ppm antioxidant	1.5–3.8	(1, 8, 20)
Tensile strength (ultimate)	MPa	$x = 1$; $R_1 = CH_3$; $R_2 = C_6H_5$; 20–50% wt. silica filler; 10–15% dibutyltin diacetate	28.6–31.4	(1, 8)
		$x = 1$; $R_1 = R_2 = CH_3$; 20–30% wt. silica filler; <3% cross-linking agent; <3 ppm antioxidant	93.8–112.4	(1, 8, 20)
Tensile strength (nominal)	MPa	$x = 1$; $R_1 = CH_3$; $R_2 = C_6H_5$; 20–50% wt. silica filler; 10–15% dibutyltin diacetate	3.9–5.9	(1, 8)
		$x = 1$; $R_1 = R_2 = CH_3$; 20–30% wt. silica filler; <3% cross-linking agent; <3 ppm antioxidant	3.5–13.0	(1, 8, 20)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Elongation at break	%	$x = 1$; $R_1 = R_2 = CH_3$; 20–30% wt. silica filler; <3% cross-linking agent; <3 ppm antioxidant	900–1,150	(1, 8)
		$x = 1$; $R_1 = CH_3$; $R_2 = C_6H_5$; 20–50% wt. silica filler; 10–15% dibutyltin diacetate	530–740	

*Onset of weight loss in dynamic TGA.

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Poly(silylenemethylene)

Q. H. SHEN AND L. V. INTERRANTE

ACRONYMS, TRADE NAMES, ALTERNATIVE NAMES PSM, PSE (**I**), HPCS, HBPSE (**II**), poly(silylenemethylene) (**I**), poly(silaethylene) (**I**), hydridopolycarbosilane (**II**)

CLASS Polycarbosilanes

STRUCTURE SiH_2CH_2

PREPARATIVE TECHNIQUES The approaches used to make poly(silylenemethylene) include ring opening polymerization (ROP) of 1,1,3,3-tetrachloro-1,3-disilacyclobutanes, followed by reduction of the Si–Cl groups with $LiAlH_4$, or a Grignard coupling reaction of Cl_3SiCH_2Cl by reduction with $LiAlH_4$. The ROP route yields a high molecular weight linear polymer (labeled **I**). The Grignard coupling gives a relatively low molecular weight polymer with a hyperbranched structure (labeled **II**).

MAJOR APPLICATIONS Precursors for SiC ceramic and SiC-matrix composites.

PROPERTIES OF SPECIAL INTEREST Relatively high cost. Very high yield for stoichiometric SiC ceramic. Viscous liquid, miscible with hydrocarbons; moderately stable in air at room temperature. Poor resistance to base and to oxidation by air at elevated temperatures (>100°C) or after a long time (several weeks) at room temperature. (These properties apply to both **I** and **II**.)

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Molecular weight	$g\,mol^{-1}$		M_n	M_w	
		Polymer **I**, gpc, PS standards	24,000	68,000	(1, 2)
		Polymer **I**, NMR	11,400	–	(2)
		Polymer **II**, po/gpc	740	1,330	(3, 4)
IR (characteristic absorption frequencies)	cm^{-1}	For linear poly(silylenemethylene) (**I**)	2,961; 2,921; 1,881; 2,130; 2,126; 1,406; 1,353; 1,250; 1,036; 946; 925; 856; 840; 756		(5)
		For branched poly(silylenemethylene) (**II**)	2,950; 2,920; 2,870; 2,140; 1,450; 1,350; 1,250; 1,040; 930; 830; 760		(3)
Raman (characteristic absorption frequencies)	cm^{-1}	For **I**	2,915; 2,875; 2,125; 2,120; 1,528; 1,356; 1,030; 983; 946; 789; 749; 706; 686; 600; 558; 472		(5)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
NMR spectra	ppm	For **I**; solution (C_6D_6)		(1, 5)
		^{1}H NMR	−0.15, 4.10	
		^{13}C NMR	−9.2	
		^{29}Si NMR	−34.4	
		For **II**; solution		(3)
		^{1}H NMR	−0.4 to 1.15; 3.55 to 4.3	
		^{13}C NMR	−12 to 9; 12.5 to 26	
		^{29}Si NMR	−66 to −53; −39 to −26; −14 to −8; 0.0 to 5	
Monoclinic cell dimensions	Å	For **I**	$a = 5.70$, $b = 8.75$, $c = 3.25$, $\gamma = 97.5$	(5)
Heat of fusion	$J\,g^{-1}$	Linear PSM	15.2	(5)
Glass transition temperature	K	Linear PSM	133–138	(6)
Melting transition temperature	K	Linear PSM	251–298	(6)
Degree of crystallinity	–	Linear PSM	70	(6)
Degree of branching	–	Linear PSM (**I**); methyl branching unit	0.5%	(2)
		Branched PSM (**II**);		(4)
		Branching units	Ratio of branching units	
		$Si(CH_2-)_4$	2	
		$SiH(CH_2-)_3$	8	
		$SiH_2(CH_2-)_2$	20	
		$SiH_3(CH_2-)$	11	
Decomposition temperatures	K	In N_2 (for both **I** and **II**)		(7)
		Starting decomp. temp.	~473	
		Ending decomp. temp.	~873	
Important patents	–	Branched PSM (**II**)	–	(8)
		Linear PSM (**I**)		(9)
Cost	–	Branched PSM (**II**)	Quoted on request from supplier	–
Availability/Supplier	g to Kg	(**II**)	Starfire Systems, Inc., Watervliet, New York	–

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Poly(silylenemethylene)

Pyrolyzability

CONDITIONS	PYROLYSIS TEMP. (K)	STRUCTURE OF CERAMIC FORMED	REFERENCE
Nature of product from linear and branched PSMs	~873 to ~1,673	Amorphous SiC	(7)
	~1,673 to ~1,873	β-SiC	
Amount of product under N_2		PYROLYSIS PRODUCT (SiC)	(7)
Linear PSM (**I**)	1,273	87%	
Branched PSM (**II**)	1,273	60–80%	
Purity of SiC		PYROLYSIS PRODUCT (SiC)	(2, 7)
Linear PSM (**I**)	1,273	1:1 stoichiometric Si to C	
Branched PSM (**II**)	1,273	SiC with slight excess of C	
Gaseous products under N_2		SUBSTANCES OTHER THAN DESIRED CERAMIC	(7)
Linear PSM	473–673	H_2 and C_2 hydrocarbons	
Deuterated PSM	473–673	D_2 and HD	

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Polystyrene

ZHENGCAI PU

ACRONYM, ALTERNATIVE NAME PS, styrofoam

CLASS Vinyl polymers

STRUCTURE $\text{-[}CH(C_6H_5)-CH_2\text{]-}$

MAJOR APPLICATIONS One of the most widely used plastics, having applications in industries of packaging, appliances, construction, automobiles, electronics, furniture, toys, housewares, and luggage.

PROPERTIES OF SPECIAL INTEREST Crystal clear thermoplastic, hard, rigid, free of odor and taste, ease of heat fabrication, thermal stability, low specific gravity, excellent thermal and electrical properties for insulating purpose, and low cost.

MAJOR PRODUCERS AND/OR SUPPLIERS Dow Chemical USA; Huntsman Chemical Corporation; BASF Corporation; Fina Oil and Chemical Company; American Polymers, Inc.; American Polystyrene Corporation; Amoco Chemicals; Arco Chemical Company; Bayer Corporation; Chevron Chemical Company; StyroChem International, Inc.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Abrasion loss factor	mg	DIN 53516	640	(5)
Birefringence dispersion	–	$\frac{\Delta n(\lambda)}{\Delta n(546\,\text{nm})}$	$A + B/\lambda^2 + C/\lambda^4$ $A = 0.8905$ $B = 0.275 \times 10^{-9}\text{cm}^2$ $C = 0.153 \times 10\text{–}18\,\text{cm}^4$	(1, 4)
Ceiling temperature	K	Gas to gas Liquid to amorphous	550 670	(5)
Characteristic ratio $\langle r^2 \rangle_0/nl^2$		$T \sim 300\,\text{K}$, various solvents	9.85	(1)
Cohesive energy	kJ mol^{-1}	–	29.6–35.4	(5)
Solvents	Benzene, carbon disulfide, cyclohexane, cyclohexanone, dimethyl phthalate, dioxane, ethyl acetate, ethylbenzene, glycol formal, methyl ethyl ketone, 1-nitropropane, phosphorus trichloride, tetrahydrofuran, tributyl phosphate			(1)
Nonsolvents	Acetone, acetic acid, alcohols, diethyl ether, diols, ethylene chlorohydrin, glycol ethers, isobutyl phthalate, phenol, saturated hydrocarbons, trichloroethyl phosphate, tricresyl phosphate			(1)

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Compressibility coefficient	bar^{-1}	$298\,K - T_g$			$2.7–4.9(\times 10^{-5})$	(2)
		$T_g - 593\,K$			$5.3–11.3(\times 10^{-5})$	
Critical heat flux, combustion	$kW\,m^2$	—			13	(2)
Density ρ	$g\,cm^{-3}$	Amorphous			1.04–1.065	(1, 4, 5)
	$g\,cm^{-3}$	Crystalline			1.111–1.127	
	$g\,cm^{-3}\,K^{-1}$	$d\rho/dT$				
		$< T_g$			-2.65×10^{-4}	
		$> T_g$			-6.05×10^{-4}	
Dielectric constant	—	At 1 kHz				
		Amorphous			2.49-2.55	(1, 4, 5)
		Crystalline			2.61	(1, 4)
Dielectric loss	—	At 1 kHz				(5)
		Amorphous			15×10^{-4}	
		Crystalline			3×10^{-4}	
Diffusion coefficient D_0	$cm^2\,s^{-1}$ $(\times 10^{-7})$	Solvent	Temp. (K)	M.W. ($kg\,mol^{-1}$)		(1)
		Acetone	293	1,200–2,450	1.18–0.80	
		Benzene	298	1.32–3.9	27.9–17.2	
		Butanone	293	180–5,500	6.4–0.81	
		Carbon tetrachloride	300	82–1,100	4.43–1.04	
		Cyclohexane	303	90	4.0	
		Cyclohexanone	298	200	5.2	
		Dioxane	303	79.8	3.10	
		Ethyl acetate	293	117–596	6.23–2.45	
		Ethyl benzene	300	770	0.96	
		Tetrahydrofuran	303	198–570	13.41–8.02	
		Toluene	293	140–2,850	4.30–0.74	
Enthalpy of fusion	$kJ\,mol^{-1}$	—			8.37–10	(1, 2, 4)
Entropy of fusion	$kJ\,K^{-1}\,mol^{-1}$	—			0.0153–0.0168	(2)
Friction coefficient	—	—			0.38	(5)
G factor	$mol\,J^{-1}$ $(\times 10^{-8})$	Cross-linking $G(X)$			7.14–19.2	(10)
		Scission $G(S)$			3.53–7.14	
Glass transition temperature	K	—			373	(2, 4, 5)

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PROPERTY	UNITS	CONDITIONS			VALUE	REFERENCE
Hardness						(5, 9)
Rockwell hardness	—	R scale			130	
		M scale			75	
Ball indention hardness	MPa	—			110	
Bierbaum scratch hardness	—	—			10.3	
Heat capacity C_p	$kJ\,K^{-1}\,mol^{-1}$	$T = 100\,K$			0.04737	(2)
		$T = 300\,K$			0.12738	(2)
					0.13258	(2)
		$T = 400\,K$			0.20124	(2)
		$T = 600\,K$			0.25430	(2)
dC_p/dT	$kJ\,K^{-2}\,mol^{-1}$	$T = 323\,K$			4.21×10^{-4}	(1, 4)
Heat conductivity	$J\,s^{-1}\,m^{-1}\,K^{-1}$	Amorphous			0.13	(5)
Heat of combustion	$kJ\,mol^{-1}$	—			-4.33×10^3	(1, 4)
Ignition temperature	K	—			675	(2)
Impact strength (Izod)	$J\,m^{-1}$	ASTM D256			19.7	(5)
Interaction parameter χ	—	Solvent	Temp. (K)	Volume fraction of polymer		(1)
		Acetone	298	0.6–1	0.81–1.1	
		Benzene	298	0.8–0.2	0.26–0.42	
		Chloroform	298	0.8–0.2	0.17–0.52	
		Cyclohexane	307	0–0.8	0.50–0.93	
		Methylcyclohexane	349	0–0.4	0.49–0.67	
		Methyl ethyl ketone	298	0.4–0.8	0.63–0.77	
		Propyl acetate	298	0.4–0.8	0.66	
		Toluene	298	1–0.2	0.16–0.37	

Interfacial tension γ_{12} (2)

Polymer pair	Temp. (K)	γ_{12} ($mN\,m^{-1}$)	$-d\gamma_{12}/dT$ ($mN\,m^{-1}\,K^{-1}$)
Polystyrene/polychloroprene	413	0.5	—
Polystyrene/poly(methyl methacrylate)	293	3.2	0.013
Polystyrene/poly(vinyl acetate)	293	4.2	0.004
Polystyrene/polyethylene	493	4.4	—
Polystyrene/poly(dimethylsiloxane)	293	6.1	~0
Polystyrene/polyethylene, linear	293	8.3	0.020

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Mark-Houwink parameters: K and a[1]

Solvent	$K \times 10^3$ (ml g^{-1})	a	Temp. (K)	M.W. range (kg mol^{-1})
Benzene	11.3	0.73	298	70–1,800
Butyl chloride	15.1	0.659	314	290–1,060
Chlorobenzene	7.4	0.749	299	620–4,240
Chloroform	7.16	0.76	298	120–2,800
Cyclohexane	82	0.50	307	10–700
Dimethylformamide	31.8	0.603	308	4–870
Dioxane	15.0	0.694	307	80–800
Ethylbenzene	17.6	0.68	298	70–1,500
Tetrahydrofuran	11.0	0.725	298	10–1,000
Toluene	12.0	0.71	303	400–3,700

Melt viscosity: molecular weight relationship constant k[4]

	Temperature (K)	Molecular weight range (kg mol^{-1})	k
Atactic	490	$\geq$38	13.04
Isotactic	554	100–600	14.42

Melt viscosity: temperature relationship constants[4]

*	$T_R = 411$ K	$T_R = 373$ K	Universal value
C_1^R	6.99	13.35	17.4
C_2^R	81.8	42.00	51.6

*$M_n = 40{,}700$ g mol^{-1}, $M_w/M_n = 2.2$.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Limiting oxygen index (LOI)	%	—	17.8	(11)
Melting point	K	—	513	(1, 4, 5)
Tensile modulus E	MPa	Unoriented	3,200–3,400	(1, 5, 9)
		Oriented monofilament	4,200	
dE/dT	MPa K^{-1}	Unoriented	−4.48	(1)
Compressive modulus	MPa	—	3,000	(4)
Shear modulus G	MPa	—	1,200	(5)
Bulk modulus	MPa	—	3,000	(5)
Flexural modulus	MPa	—	3,100	(5)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Optical dispersion $\eta_F - \eta_C$	—	$\lambda = 486.1$ nm $\lambda = 656.3$ nm	1.92×10^{-2}	(4, 12)
Permeability coefficient	m^3 (STP) m s^{-1} m^{-2} Pa^{-1}	$T = 298$ K; permeant = H_2 He N_2 O_2 H_2O CO_2	 17.0×10^{-4} 14.0×10^{-4} 0.59×10^{-4} 2.0×10^{-4} 840×10^{-4} 7.9×10^{-4}	(1)
Poisson ratio	—	—	0.325–0.33	(1, 4, 5)
Refractive index n dn/dT	 K^{-1}	$\lambda = 589.3$ nm	1.59–1.60 -1.42×10^{-4}	(1, 4)
Refractive index increment dn/dc	ml g^{-1}	Various solvents	0.103–0.225	(1)
Resistivity	ohm cm		10^{20}–10^{22}	(1, 4)
Scattering length density r_n	cm^{-2}	Neutron	1.415×10^{10}	(2)

Second virial coefficient A_2 (1)

Solvent	$A_2 \times 10^4$ (mol cm^3 g^{-2})	Temp. (K)	Molecular weight (kg mol^{-1})
Benzene	3.3–3.6	293	7,100–1,330
Bromobenzene	2.15–6.38	293	1,750–35.5
Butanone	0.0127	293	150
Carbontetrachloride	3.58	293	150
Chloroform	6.56	—	—
Dioxane	2.75	—	—
Methyl acetate	−0.235	303	179.3
1-Phenyldecane	−3.22	295	390
Toluene	1.37–2.32	293	40,200–12,300

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Solubility parameter	$(MPa)^{1/2}$	Various solvents	15.6–21.1	(1, 5, 13)
Sound absorption, longitudinal	$dB\ cm^{-1}$	RT, 2 MHz	1.4	(14)
Speed of sound		RT, 1 MHz		(2)
Longitudinal C_L	$m\ s^{-1}$		2,400	
$-dC_L/dT$	$m\ s^{-1}\ K^{-1}$		1.5	
$dC_L/d\log f$	$m\ s^{-1}\ dec^{-1}$		1.4	
$d\ln C_L/dP$	GPa^{-1}		0.9	
Shear C_S	$m\ s^{-1}$		1,150	
$-dC_S/dT$	$m\ s^{-1}\ K^{-1}$		4.4	
$d\ln C_S/dP$	GPa^{-1}		0.5	
Stress-optical coefficient (brewsters)	—	Monofilament	10.1	(1, 4)
		Extruded sheet	9.5	
		Compression molded	8.3–8.7	

Surface tension γ $(mN\ m^{-1})$[1]

Molecular weight $(g\ mol^{-1})$	Temperature (K)			$-d\gamma/dT$ $(mN\ m^{-1}\ K^{-1})$
	293	423	473	
$M_v = 44{,}000$	40.7	31.4	27.8	0.072
$M_n = 9{,}300$	39.4	31.0	27.7	0.065
$M_n = 1{,}700$	39.3	29.2	25.4	0.077

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Thermal conductivity	$W\ m^{-1}\ K^{-1}$	$T = 273$ K	0.105	(1, 2, 4)
		$T = 323$ K	0.116	(1, 2, 4)
		$T = 373$ K	0.128	(1, 2, 4)
		$T = 473$ K	0.13	(2)
		$T = 573$ K	0.14	(2)
		$T = 673$ K	0.160	(2)
Thermal decomposition	K	Initial temperature	573	(2)
		Half decomposition temperature	637	
Thermal expansion coefficient	K^{-1}	Linear		(1, 4)
		$<T_g$	6–8 $(\times 10^{-5})$	
		Volume		
		$<T_g$	1.7–2.1 $(\times 10^{-4})$	
		$>T_g$	5.1–6.0 $(\times 10^{-4})$	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Theta temperature Θ	K	Solvent		(1)
		i-Butyl acetate	227	
		n-Butyl formate	264	
		1-Chlorodecane	279	
		1-Chlorododecane	332	
		1-Chloroundecane	306	
		Cyclohexane	307–308	
		Cyclohexanol	352–361	
		Cyclopentane	293	
		Decalin	285–304	
		Diethyl malonate	304–309	
		Diethyl oxalate	325–333	
		Ethyl acetoacetate	381	
		Ethylcyclohexane	343	
		Methylcyclohexane	333–343	
		3-Methylcyclohexanol	371	
		1-Phenyldecane	301-304	
Tensile strength at break	MPa	—	30–60	(2)
Elongation at break	%	—	1–4	(2)
Flexural strength	MPa	—	95	(5)
Compressive strength	MPa	—	95	(5)
Unit cell		Isotactic		(1, 4)
Crystallographic system	—		Rhombohedral	
Space group	—		D3D-6	
Cell dimension	Å		$a_0 = 21.9–22.1$	
			$b_0 = 21.9–22.1$	
			$c_0 = 6.65–6.63$	
Repeat unit per unit cell	—		18	
Upper use temperature	K	—	333	(2)
Vicat softening point	K	—	373	(4)
Zisman critical surface tension	$mN\,m^{-1}$	—	32.8	(15)

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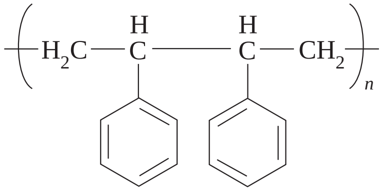
Polystyrene, head-to-head

MICHAEL. T. MALANGA

ACRONYMS H-H PS, H-H polystyrene

CLASS Chemical copolymers

STRUCTURE $[-CH_2-CH(C_6H_5)-CH(C_6H_5)-CH_2-]$



PREPARATIVE TECHNIQUE H-H polystyrene has never been obtained directly from styrene monomer. It is synthesized by the selective hydrogenation of 1,4-poly(2,3-diphenyl-1,3-butadiene) (PDPB) using potassium/ethanol. PDPB is prepared by the free radical polymerization of 2,3-diphenyl-1,3-butadiene to give a 45% *cis*, 55% *trans* structure. H-H PS is then given in the same ratio of erythro and threo linkages after the chemical reduction of the internal double bond of the PDPB.[1,2]

MAJOR APPLICATIONS This polymer is not manufactured commercially by any company in the world at this time. It has only been prepared in laboratory scale quantities. The primary reason for this is that the cost of preparing H-H polystyrene would be very high for the perceived value of its properties. There are no published reports of the mechanical properties of H-H polystyrene at this time. However, given its measured glass transition temperature and backbone structure it may be anticipated to have similar tensile, modulus, and other mechanical properties to commercial H-T polystyrene.

PROPERTIES OF SPECIAL INTEREST H-H PS is completely miscible with poly(2,6-dimethyl phenylene oxide) in the same way that H-T PS is miscible with that polymer.[3] The T_g of the blends are then intermediate between the two polymers. The thermal stability and glass transition temperature of H-H PS are very similar to those of atactic H-T PS despite the structural differences.[1] Although the H-H linkage has been suggested as a possible "weak link" in the commonly manufactured H-T polystyrene, the thermal stability evidence suggests that this is not the case.[4]

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PROPERTY	UNIT	CONDITIONS	VALUE	REFERENCE
Preparation (see above) hydrogenation of 1,4-poly (2,3-diphenyl-1,3-butadiene)	Radical polymerization of 2,3-diphenyl-1,3-butadiene followed by chemical reduction of the internal double bond yields the H-H polystyrene structure			(1, 2)
Structural analysis: ^{13}C NMR	Chemical shift in ppm relative to TMS	30% solution in chlorobenzene at 90°C Phenyl 1 carbon Methine backbone carbon Methylene backbone carbon	 144.3 49.7 28.9	(1, 5)
Glass transition temperature	K	DSC with heating rate of 10°C min^{-1}	370	(1)
Thermal decomposition temperature	K	DTG onset of degradation, 10°C heating rate, under nitrogen	620	(1)
Theta temperature	K	Cyclohexane solvent	292	(6)
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None	THF solvent at 25°C	$K = 5.3 \times 10^{-2}$ $a = 0.61$	(6)
Second virial coefficient A_2	mol cm^3 g^{-2}	Cyclohexane solvent at 35°C, 82,800 weight average molecular weight	2.3×10^{-4}	(6)
Interaction parameter	–	THF solvent at 25°C Cyclohexane at 35°C	0.464 0.471	(6)
Crystallinity	The polymer shows no crystallinity. It is considered completely amorphous.			(4)

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Poly(sulfur nitride)

J. F. RUBINSON AND HARRY B. MARK, JR.

ACRONYM, ALTERNATIVE NAME $(SN)_x$, polythiazyl

CLASS Inorganic and semi-inorganic polymers

STRUCTURE [⋯S⋯N⋯]

MAJOR APPLICATIONS Electrode fabrication in crystalline, film, or paste form. Electrodes are useful in both aqueous and some nonaqueous solvents. Ion-selective electrode. Contact with semiconductors yields high-voltage junction. Photocell fabrication.

PROPERTIES OF SPECIAL INTEREST A number of the intermediates in its synthesis as well as the dry polymer are explosive under certain conditions. A thorough literature survey of its properties should be undertaken before synthesis or use.[1,2] Intrinsic metallic conductor. Undoped polymer is a superconductor at 0.3 K, while doped forms have been made with higher T_c.

PROPERTY	UNITS	CONDITIONS	VALUES					REFERENCE
Electrochemical breakdown potential ($|i| \geq 0.02\,mA\,cm^{-2}$)	V vs. SCE	0.1 M electrolyte: Solvent	Et_4NClO_4	$LiClO_4$	Me_4NClO_4	LiCl		(3)
		Ethanol	–	–	−0.51	−0.57		
		Propylene carbonate	−0.48	−0.81	–	–		
		Acetonitrile	−0.40	−0.74	–	–		
		Solvent	Et_4NClO_4	$LiClO_4$	Me_4NClO_4	LiCl		
		Ethanol	–	–	+0.80	+0.82		
		Propylene carbonate	+0.87	+0.80	–	–		
		Acetonitrile	+0.95	+0.96	–	–		
Electrochemical breakdown potential ($|i| \geq 1.0\,mA\,cm^{-2}$)	V vs. SCE	0.1 M electrolyte: Breakdown type	LiCl	NaCl	$KClO_4$	KPF_6	Et_4NClO_4	(4)
		Cathodic breakdown	−3.6	−3.6	−3.6	−3.6	−3.3	
		Anodic breakdown	2.2	2.2	2.2	3.2	2.1	

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Poly(sulfur nitride)

Preparative techniques

Technique	Conditions	Reference
Plasma	He plasma, S_4N_4 vapor	(5)
Solution phase	$N_3^- + S_aN_bCl_c$ in acetonitrile (−258 K)	(6)
Solution phase	$N_3^- + S_2NAsF_6$ in liquid SO_2 (−20°C)	(6)
Vapor phase	S_4N_4 sublimation over Ag wool; S_2N_2 trapped at 77 K, then 273 K; polymerization at temperature	(7)
Solution phase	$(NSCl)_3 + Me_3SiN_3$ in liquid SO_3 (−18°C)	(8)
Electrochemical	S_5N_5Cl in liquid SO_2	(9)
Photopolymerization	S_4N_4 decomposition products, irradiated with γ up to visible range	(10)

IR (characteristic absorption frequencies)

	Wavelength (cm^{-1})										Reference
KBr pellet	1,400	1,225		1,010	930	690		600			(5)
Nujol mull	1,400	1,225	1,047	1,015		685	657	600			(11)
Nujol mull					1,000	693	635		500	285	(8)
Film on KBr					1,002	685	625		500, 467	283	(8)

Unit cell dimensions[12]

Lattice	Monomers per units cell	Cell dimensions (Å)			Cell angle (degrees)
		a	*b* (chain axis)	*c*	β
Monoclinic ($P2_1/c$)	4 (N-S)	4.153	4.439	7.637	109.7

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Electrical conductivity σ	$S\,cm^{-1}$	|| *b*-axis, 300 K ⊥ to *b*-axis, 300 K	2,000 40	(12)
$\sigma_{\|\|}/\sigma_{\perp}$	–	Room temperature 20 K	50 500–1,000	(1)
Electronegativity	–	–	2.9	(12)
Decomposition temperature	K	–	513	(1)
Enthalpy of vaporization	$kJ\,mol^{-1}$	–	135.9	(1)
Entropy of vaporization	$kJ\,K^{-1}\,mol^{-1}$	–	0.3388	(1)
Conduction bandwidth	eV	–	2–3	(1)
Young's modulus	MPa	Crystal	3×10^{-16}	(1)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Yield stress	MPa	Crystal	1.450×10^2	(1)
Breaking stress	MPa	Crystal	3.660×10^2	(1)
Specific heat	–	<3.2 K 4–20 K >20 K	$C/T = \text{constant} \times T^3$ $C/T = \text{constant} \times T^{2.7}$ $C = \text{constant} \times T$	(1)
Magnetic susceptibility	emu g^{-1}	Crystal	$(0.2 \times 0.1) \times 10^{-6}$	(1)
Paramagnetic susceptibility	emu mol^{-1}	Crystal	$(5.5–1.0) \times 10^{-6}$	(1)
Drude edge ($R_{\|\|}$ vs. $\nu \times 10^{-3}$)	cm^{-1}	Oriented film or crystal	20,000	(13)
Density	g..cm^{-3}	Crystal	2.3	(1)

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Poly(tetrafluoroethylene)

D. L. KERBOW

ACRONYM, TRADE NAMES PTFE, Teflon, Hostaflon, Fluon, Algoflon, Halon, Polyflon, Fluoroplast

CLASS Poly(α-olefins)

STRUCTURE $[-CF_2-CF_2-]$

MAJOR APPLICATIONS Granular and fine powder forms are used in electrical wire insulation, seals, and gaskets, and in valve and pipe fittings and linings for harsh chemical applications. Fine powders are also prepared in fiber, filament, and porous fabric forms. Dispersions are used in glass cloth coatings to provide weather protection, mechanical strength, and chemical resistance. Micropowders are used as additives to inks, lubricants, and plastics to provide lubricity, antiburning, and nonstick properties.

PROPERTIES OF SPECIAL INTEREST Three major forms of PTFE exist: granular, fine powder, and micropowders. Granular is produced by suspension polymerization in the absence of a surfactant. It is a spongy, porous form of irregular particle shape as polymerized, and it is typically ground to a particle size to suit fabrication and end-use needs. Fine powder is coagulated from dispersion which is polymerized in the presence of an emulsifying agent. It can be supplied as the dispersion or in a coagulated form. It is extremely sensitive to mechanical shear. Micropowder can be produced as a low molecular weight form of fine powder or by scission of fine powder products by gamma or electron beam irradiation. It is typically a waxy or friable powder.

CRYSTALLINE REPEAT UNIT The polymer chain in the crystalline matrix exists as a helix, with successive CF_2 units rotated slightly by the steric interference of adjacent fluorine atoms. The repeat distance of the helix is 19.5 Å (15 CF_2 units) at temperatures above 19°C, or 16.9 Å (13 CF_2 units) below 19°C.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	50.01	—
Tacticity	—	—	None	—
Degree of branching	—	—	None	—
Typical molecular weight range	$g\,mol^{-1}$	Polymer form		(1)
		Fine powder	$1–5 \times 10^7$	
		Granular	10^7	
		Micropowder	$2–25 \times 10^4$	

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
IR (characteristic absorbances frequencies)	cm^{-1}	Assignment	Strength		
		Overtone (1,152 + 1,213): used analytically as a "thickness band"	Very strong	2,367	(2) (Ch. 21)
		–	Very strong	1,242	(2)
		–	Very strong	1,213	(2)
		CF_2 stretch	Very strong	1,152	(2)
		Crystallinity: used analytically to determine % C as noted below	Weak	778	(3)
		C–C–F bend	Strong	638	(2)
		CF_2 bend	Strong	553	(2)
		C–C–F bend	Strong	516	(2)
Coefficient of linear thermal expansion (average)	$K^{-1} \times 10^{-6}$	298–83 K		86	(4)
		298–173 K		112	
		298–273 K		200	
		296–333 K (ASTM D696)		120	
		298–373 K		124	
		298–473 K		151	
		298–573 K		218	
Compressibility	bar^{-1}	Calculated		28.8×10^{-18}	(4)
Solubility parameter	$(MPa)^{1/2}$	Calculated		12.7	(2) (Ch. 16)
Solvents	–	>573 K		Perfluorinated materials	(4)

Crystalline state properties: PTFE exists in multiple forms that are influenced by temperature, pressure, and thermal history. In turn, these forms significantly influence the physical, electrical, and processing properties of the polymer. Particularly, the percent crystallinity and specific gravity have been found to relate to a large number of properties, and since these parameters are influenced by processing history, it is very important to specify precise sample preparation conditions. In equations below, % C = percent crystallinity, and ρ = density.

Crystal lattice

Crystalline form	Conditions	Unit cell dimensions (nm)			λ (degrees)
		a	*b*	*c*	
Form I	Above 30°C	0.567	0.567	>1.950	–
Form II	Below 19°C	0.559	0.559	1.688	119.3
Form III	High pressure	0.873	0.569	0.262	–
Form IV	19–30°C	0.566	0.566	1.950	–

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Crystal lattice (*continued*)[5]

Crystalline form	Chain conformation	Space group	Crystal density
Form I	15/7	Trigonal ($P3_1$ or $P3_2$)	2.35
Form II	13/6	Triclinic (pseudohexagonal)	2.30
Form III	2/1	Orthorhombic (Pnam)	2.55
Form IV	15/7	Trigonal ($P3_1$ or $P3_3$)	2.74

PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Entropy of fusion	$kJ\,K^{-1}\,mol^{-1}$	D4591 (ASTM method)		0.477	(4)
Degree of crystallinity	$g\,cm^{-3}$	–		762.5-(1,524.5/ρ)	(4)
Heat of fusion	$kJ\,kg^{-1}$	D4591 (ASTM method)		82	(4)
Density	$g\,cm^{-3}$	Crystal state			
		Completely amorphous, 298 K		2.0 (calculated)	(4)
		Triclinic, < 292 K		2.344	(4)
		Hexagonal, 298 K		2.302	(4)
		As polymerized, 298 K		2.280–2.290	(4)
		Melt, 653 K		1.46	(2) (Ch. 24)
Melting point	K		Polymer form		(4)
		Irreversible	As polymerized	608–618	
		Reversible	Second (and subsequent) melting	600	
		–	Equilibrium	586.9	
		Irreversible	Extended chain	658	
Transition temperature	K		Type of transition		(4)
		–	Alpha (glass I)	399	
		Crystalline, crystal disordering relaxation	Beta	292	
		Crystal disordering	Beta II	303	
		–	Amorphous 2nd order	243	
		Onset of rotation around C–C bond	Gamma (glass II)	193	

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Heat capacity	$kJ\,kg^{-1}\,K^{-1}$		Crystalline	Amorphous	(4)
		DSC, 10 K	1.228		
		100 K	19.37	19.37	
		300 K	45.09	51.42	
		500 K	61.62	66.05	
		605 K (melting point)	67.88	69.54	
		700 K	73.30	72.69	
Deflection temperature	K	Deflection force (MPa – D648)			(4)
		0.455	405		
		1.82	333		
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	C177	$(4.86 \times 10^{-4})\,T + 0.253$		(4)
Tensile modulus	MPa	22 K (ASTM D638)	4,100		(4)
		77 K	3,400		
		144 K	2,500		
		200 K	1,800		
		296 K	340		
		373 K	69		
Tensile strength	MPa		Granular	Fine powder	
		298 K	7–28	17.5–24.5	(1)
		298 K	–	270–0.39 (% C) – 99.3ρ	(4)
Yield stress	MPa	22 K (ASTM D638)	131		(4)
		77 K	110		
		144 K	79		
		200 K	53		
		296 K	10		
		413 K	5.5		
		523 K	3.4		
Modulus type		ASTM D 695			(4)
Compressive	MPa	After 100 h at 6.895 MPa, 23°C	186		
Tensile		–	61		
Flexural		–	$2{,}814 - 158.5\,(\%\ C) + 2.919\,(\%\ C)^2 - 0.1638\,(\%\ C)^3$		
Maximum extensibility	%	ASTM D638	Granular	Fine powder	
		22 K	–	2	(4)
		77 K	–	6	(4)
		144 K	–	90	(4)
		200 K	–	160	(4)
		296 K	100–200	200–600	(1)

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Flexural modulus	MPa	ASTM D790	Granular	Fine powder	
		22 K	–	5,200	(4)
		77 K	–	5,000	(4)
		144 K	–	3,200	(4)
		296 K	350–630	280–630	(1)
		328 K	–	400	(4)
		373 K	–	190	(4)
Flexural strength	MPa	D790	No break		(4)
Impact strength	$J\,m^{-1}$	D256 (notched Izod impact)			(4)
		216 K	107		
		276 K	187		
		350 K	>320		
Hardness	Shore D	D2240	$42 + 0.2$ (% C)		(4)
Plateau modulus	MPa	653 K	1.7		(2) (Ch. 24)
Entanglement molecular weight	$g\,mol^{-1}$	–	3.7×10^3		(2) (Ch. 24)
Index of refraction	–	η_D^{25}	1.376		(4)
Dielectric constant ε	–	D150	2.1		(4)
Dielectric strength	$V\,mm^{-1}$	D149	2.36×10^4		(1)
Dissipation factor	–	D150 (60 Hz to 2 GHz)	$< 3 \times 10^{-4}$		(4)
Resistivity, surface	$ohms\,sq^{-1}$	D257 (100% RH)	3.6×10^6		(4)
Resistivity, volume	ohms cm	D257 (50% RH)	10^{19}		(4)
Surface tension	$mN\,m^{-1}$	293 K	25.6		(2) (Ch. 48)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	298 K	0.25		(2) (Ch. 10)
Coefficient of sliding friction	–	D 1894	$0.244\,W^{0.163}$ (W = load in grams)		(4)
Static coefficient of friction	–	Against polished steel	0.05–0.08		(1)
Speed of sound	$m\,sec^{-1}$	1 MHz, 298 K			(2) (Ch. 49)
		Longitudinal	1,410		
		Shear	730		
Ignition temperature	K	–	767		(2) (Ch. 42)

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Weight loss in air	% h^{-1}		Granular	Fine powder	(4)
		505 K	$1–5 \times 10^{-5}$	1×10^{-4}	
		533 K	$1–2 \times 10^{-4}$	6×10^{-4}	
		589 K	5×10^{-4}	5×10^{-3}	
		644 K	4×10^{-3}	3×10^{-2}	
Pyrolysis products	mol %	Vacuum at 783 K			(6)
		CF_4	0.86		
		C_2F_4	93.97		
		C_3F_6	2.55		
		cyclo-C_4F_8	0.73		
Maximum use temperature	K	In air	533		(1)
Depolymerization rate	g sec^{-1}	Vacuum pyrolysis	$3 \times 10^{-19}\,M^{(-83{,}000/RT)}$		(7)
Water absorption	%	D570	0.0		(4)
Flammability	–	UL 94	VE-0		(4)
	%	D2863 (Limiting oxygen index)	>95		(4)
Cost	US$ kg^{-1}	–	11–35		
Availability	37,000 metric tons in 1994				
Suppliers	Asahi Glass, Ausimont, CIS, Daikin Kyogo, DuPont, and Hoechst				

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Poly(tetrahydrofuran)

QINGWEN WENDY YUAN

ACRONYM PTHF

CLASS Polyethers

STRUCTURE $[-CH_2-CH_2-CH_2-CH_2-O-]$

PROPERTY	UNITS	CONDITIONS		VALUES	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—		72	—
Polymerization	—	—		Cationic ring-opening living polymerization	(1–3)
Solvents	Benzene, ethanol, tetrahydrofuran, chloroform				(4–6)
Nonsolvents	Petroleum ether, hexane, methanol, water				(4–6)
Theta temperature	K	Solvent*	Method†		
		Acetonitrile/benzene (61.5/38.5)	CP	298.5	(6, 7)
		Acetonitrile/butanone (38.3/61.7)	CP	298.5	(6, 7)
		Acetonitrile/carbon tetrachloride (50.2/49.8)	CP	298.5	(6, 7)
		Acetonitrile/chlorobenzene (60.1/39.9)	CP	298.5	(6, 7)
		Acetonitrile/tetrahydrofuran (58.7/41/3)	CP	298.5	(6, 7)
		Acetonitrile/toluene (61/39)	CP	298.5	(6, 7)
		n-Butanol	PE	278.5	(1, 6)
		Butanone	VM	298.5	(6)
		Chlorobenzene	VM	298.5	(6)
		Chlorobenzene/*n*-octane			
		(25.0/75.0)	A, CP	283.5	(6, 8)
		(21.5/78.5)	A, CP	299.3	(6, 8)
		(14.5/85.5)	A, CP	319.5	(6, 8)
		(13.0/87.0)	A, CP	336.5	(6, 8)
		(10.9/89.1)	A, CP	353.5	(6, 8)
		Cyclohexane/*n*-heptane	—	299.5	(6)
		Diethyl malonate	PE	307.0	(6, 9)
		Ethyl acetate/*n*-hexane (22.7/77.3)	PE	303.9	(6, 9)
			A	306.5	(6, 10)
		i-Propanol	PE	318.1	(6, 9)
		Toluene	A	301.8	(6, 11)

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PROPERTY	UNITS	CONDITIONS	VALUES		REFERENCE
Second virial coefficient	mol cm^3 g^{-2} ($\times10^{-4}$)	Ethyl acetate, $T = 30°C$, $M_w \times 10^{-3} = 34.6–1,030$ g mol^{-1}	6.14–2.47		(6, 10)
Mark-Houwink parameter: K and a	K = ml g^{-1} a = None	Mol. wt. = (3.5×10^4) to (1.1×10^6) g mol^{-1}	K	a	
		Benzene, 30°C	131×10^{-3}	0.60	(6, 10)
		Cyclohexane, 30°C	176×10^{-3}	0.54	(6, 10)
		Ethyl acetate, 30°C	422×10^{-4}	0.65	(6, 10)
		Ethyl acetate/n-hexane (22.7/77.3 by weight), 31.8°C	343×10^{-3}	0.45	(6, 10)
		Toluene, 28°C, $(3–12)\times10^4$ g mol^{-1}	25.1×10^{-3}	0.78	(6, 11)
Density	g cm^{-3}	Amorphous at 25°C	0.975		(12)
		Amorphous	0.982		(6, 13)
		Crystalline at 25°C	1.07–1.08		(12)
		Crystalline	1.157		(6)
		Crystalline	1.112		(6, 14)
		Crystalline	1.116		(6, 13)
		Crystalline	1.238		(6)
		Crystalline	1.095		(6, 15)
Avrami exponent	–	IR	2.2		(16)
		DSC	2.4		
Glass transition temperature	K	–	187.5		(12)
			189		(6, 17, 18)
			189.5		(19)
Melting temperature	K	–	316.5		(12, 19)
			331.5–333.5		(12)
Heat capacity	kJ K^{-1} mol^{-1} ($\times10^{-3}$)	Temp. (K)	Solid	Melt	(6, 20, 21)
		10	1.47	–	
		20	6.59	–	
		30	12.42	–	
		40	18.32	–	
		50	24.63	–	
		60	29.74	–	
		70	34.61	–	
		80	39.41	–	
		90	43.67	–	
		100	47.27	–	
		110	50.72	–	
		120	54.70	–	
		130	57.99	–	
		140	61.12	–	
		150	64.46	–	
		160	67.96	–	

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PROPERTY	UNITS	CONDITIONS	VALUES		REFERENCE
Heat capacity	kJ K^{-1} mol^{-1} ($\times 10^{-3}$)	Temp. (K)	Solid	Melt	(6, 20, 21)
		170	71.20	–	
		180	74.52	–	
		190	–	124.20	
		200	–	125.92	
		210	–	127.64	
		220	–	129.36	
		230	–	131.09	
		240	–	132.81	
		250	–	134.53	
		260	–	136.26	
		270	–	137.98	
		280	–	139.70	
		290	–	141.42	
		300	–	143.15	
		310	–	144.87	
		320	–	146.59	
		330	–	148.32	
		340	–	150.04	
Tensile strength	MPa	High molecular weight	29.0		(12)
		Low to high molecular weight	27.6–41.4		
		Cured	16.8–38.3		
		Cured plasticized high molecular weight	13.7–19.0		
Elongation	%	High molecular weight	820		(12)
		Low to high molecular weight	300–600		
		Cured	400–740		
		Cured plasticized high molecular weight	450–735		
Modulus of elasticity	MPa	–	97.0		12)
Engineering modulus	MPa	Elongation = 300%			(12)
		Low to high molecular weight	1.6–4.3		
		Cured plasticized high molecular weight	13.7–19.0		
Hardness	Shore A	–	95		(12)
Thermal expansion coefficient	K^{-1}	$\alpha = (1/V)(\delta V/\delta T)_p$	$(4–7) \times 10^{-4}$		(12)
Compressibility	kPa^{-1}	$\beta = (1/V)(\delta V/\delta p)_T$	$(4–10) \times 10^{-7}$		(12)
Internal pressure	MPa	–	281		(12)
Coefficient of expansion dV_s/dT	cm^3 g^{-1} K^{-1}	–	7.3×10^{-4}		(12)
Index of refraction	–	20°C	1.48		(12)
Dielectric constant ε	–	20°C	5.0		(12)

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PROPERTY	UNITS	CONDITIONS		VALUES			REFERENCE
Specific refractive index increment *dn/dc*	$ml\,g^{-1}$	Solvent	Temp. (°C)	$\lambda_0 = 436\,nm$	$\lambda_0 = 546\,nm$		(6)
		Chlorobenzene	—	0.070	—		
		Ethyl acetate	25	0.110	—		
			30	0.114	—		
		Ethyl acetate/*n*-hexane (22.7/77.3 wt)	31.8	0.114	—		
		Isopropanol	46	0.108	—		
		Isopropyl acetate	22.5	0.098	—		
		MEK	30	0.102	—		
			25	0.091	—		
				0.095	—		
		Methyl acetate	25	0.101	—		
		3-Methyl-2-heptanone	25	0.056	—		
		2-Pentanone	25	0.084	—		
		THF	25	0.0625	0.0625		
				0.064	—		
Surface tension	$mN\,m^{-1}$			20°C	150°C	200°C	
		$M = 43{,}000\,g\,mol^{-1}$		31.9	24.0	20.9	(6, 22, 23)
		$M = 2{,}500\,g\,mol^{-1}$		38.2	27.9	24.0	(6)

*Numbers in parenthesis are compositions in volume/volume.
†CP = cloud point titration; PE = phase equilibria; VM = intrinsic viscosity/molar mass; A = virial coefficient.

Fractionation[6]

Method	Solvent	Nonsolvent
Fractional precipitation	Acetone	—
	Benzene	*n*-Hexane
	Benzene	Methanol
	Toluene, methanol	—
Tribidimetric titration	Ethanol	Water
Distribution between immiscible liquids	Cyclohexane-toluene (9:1)	Water-methanol
Extraction	Water	Acetone
	Isopropanol	Water
Fractional solution	2-Butanone	—
	Isopropanol	Water
	Ethyl ether	Petroleum ether
Chromatography	Acetone	Water
	2-Butanone	—
	Dimethylformamide	—
	Methanol-water mixture	—
	Tetrahydrofuran	—
	Toluene	—
Sedimentation velocity	Ethyl acetate-*n*-hexane (22.3/77.7)	—

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Poly(tetrahydrofuran)

Crystalline-state properties

Lattice	Space group	Unit cell parameters (Å)			Angles (degrees)	Monomers per unit cell	Reference
		a	*b*	*c*			
Monoclinic	C2H-6	5.48	8.73	12.07	$B = 134.2$	4	(1)
Monoclinic	C2H-6	5.59	8.90	12.07	$B = 134.2$	4	(1, 14)
Monoclinic	—	—	8.89	12.15	—	—	(1, 13)
Orthohombic	D2-4	12.2	8.75	7.22	—	8	(1)
Monoclinic	C2H-6	5.61	8.92	12.25	$B = 134.5$	4	(1, 15)
Monoclinic	—	5.48–5.61	8.73–8.92	12.97–12.25	$B = 134.2–134.5$	—	(12)

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Polythiophene

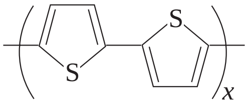
SHRISH RANE AND GREG BEAUCAGE

ACRONYM PT

CLASS Polyheterocyclics; conjugated conducting polymers

STRUCTURE Polythiophene exists in two structures:

(Aromatic)



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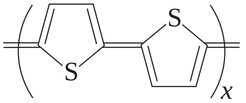

MAJOR APPLICATIONS Polythiophenes and the substituted polythiophenes are utilized in a variety of applications where their conducting properties pose an advantage. They are presently used as antistatic coatings and films. Research is being done to explore their use in electrochromic and electroluminescent devices. They have also shown some promise as material for biosensors and storage batteries. Used in making Schottky barrier diodes and field effect transistors.

PROPERTIES OF SPECIAL INTEREST Presence of an extended π-bonding system, which imparts electrical properties to the polymer. Doping either p or n can enhance these properties. First among their class to be stable to moisture and oxygen in both their doped and undoped states. They also exhibit other interesting properties such as electrochromism, thermochromism, and pressure induced color change.

PROPERTY	CONDITIONS	REFERENCE
Chemical synthesis	Polycondensation reaction of di-functional thiophene in presence of Ni catalysts Oxidative coupling reaction of bi-thiophene in presence of ferric chloride using $AlCl_3$, $CuCl_3$ and organic solvents Plasma polymerization from 3-methyl thiophene or thiophene	(1–6)
Electrochemical synthesis	Electrodes (platinum, gold, and Au coated Ni) Electrolytes (acetonitrile in tetra-alkylammonium, iodide salts, fluoroborate salts, Bu_4N^+, Et_4N^+, and quaternary ammonium salts	(1, 2, 7–11)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Conductivity	$S\,cm^{-1}$	Iodine doped	6–8	(4, 11)
		$FeCl_3$ doped	0.5	(11)
		$NOSbF_6$ doped	9×10^{-5}	(12)
		$NOPF_6$ doped	2×10^{-5}	(12, 13)
		$SO_3CF_3^-$ doped	50–100	(14, 15)

PROPERTY	CONDITIONS	REFERENCE
Chromisms		
Thermochromism	Two types:	
	An abrupt shift from planar back-bone to a twisted form at high temperatures	(16)
	A continuous modification in the back-bone with increasing temperature	(17, 18)
Electrochromism	The vis-spectra shows a change during the doping/dedoping process	(19)
Solvatochromism	Chain conformation changes from nonplaner in solid state to coplaner in solution	(20–22)
Ionochromism	Polymer displays an absorption shift with K^+, Na^+, Li^+	(23–26)
Pressure, light, and electricity induced color changes	PT and its derivatives show different molecular forms under the influence of pressure, light, and electricity	(17, 28)
Optical properties	PT and its derivatives display photoluminescence and electroluminescence	(29, 31)
Magnetic properties	PTs show variation in their magnetic properties. In the doped state they undergo transition from a paramagnetic state at high temperature to an ordered phase at low temperatures.	(32, 33)
Solubility	PT by itself is insoluble and infusible. Substitution of alkyl units in the 3-position and copolymers of PT increase the solubility and ease of processability, the penalty being some decrease in its conductivity.	(1, 2, 14, 34)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Thermal stability	K	In air	523	(1)
		In inert atmosphere or vacuum	1,173	
UV-Vis spectroscopy	nm	Strong absorption band in doped state	480	(1, 14)
IR properties	cm^{-1}	C=C stretch		(1, 2, 14)
		Chemical synthesis PT	1,494	
		Electrochemical synthesis PT	1,490	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
IR properties	cm^{-1}	C–H (in-plane bend)		
		Chemical synthesis PT	1,052	
		Electrochemical synthesis PT	1,058	
		C–H (out-of-plane bend)		
		Chemical synthesis PT	788	
		Electrochemical synthesis PT	785	
		C_γ–H		
		Chemical synthesis PT	690	
		Electrochemical synthesis PT	690	
		ν cycle		
		Chemical synthesis PT	1,400	
		Electrochemical synthesis PT	1,408	
		ν cycle		
		Chemical synthesis PT	1,230	
		Electrochemical synthesis PT	1,226	
Crystallinity	PTs appear completely amorphous under XRD scans. Substituted PTs display partial degrees of crystallinity (<5%)			–
Hexagonal lattice	Å	–	$a = 9.5$, $c = 12.2$	(1)
Density	$g\,cm^{-3}$	–	1.4–1.6	(1)
Morphology	Main determining parameters are monomer structure, dopant, and thickness of film TEM images of PT films display fibrillar, ''noodle-like'' structure. Fibril diameter increases with doping level			(1, 35)

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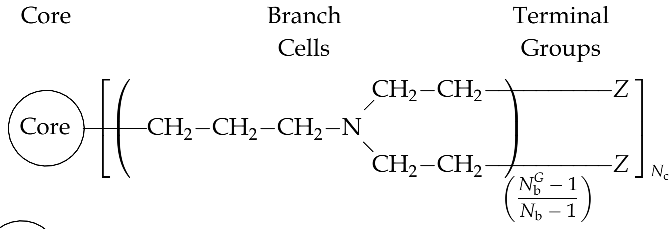
Poly(1,3-trimethyleneimine) dendrimers

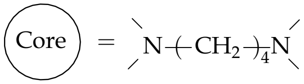
DONALD A. TOMALIA AND MARGARET ROOKMAKER

ALTERNATIVE NAME, ACRONYM, TRADE NAME Polypropylenimine (POPAM) dendrimers, Astramol® dendrimers

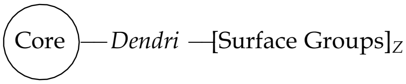
CLASS Dendritic polymers; dendrimers

STRUCTURE Dendrimers are three-dimensional macromolecules consisting of three major architectural components: a core, branch cells, and terminal groups. These products are constructed from repeat units called *branch cells* [e.g., $-CH_2-CH_2-CH_2-N(CH_2-CH_2-CH_2)_2$] in concentric generations (G) surrounding various cores according to dendritic rules and principles, where N_c = multiplicity of core; N_b = multiplicity of branch cell; and Z = terminal groups (i.e., $-CN$ or $-CH_2-NH_2$).



where 

DSM uses its own designation to describe these dendritic products, wherein the three architectural components are noted as follows:



where the core is diaminobutane (DAB) (i.e., 1,4-diaminobutane); *dendri* indicates the interior dendritic branch cell; and the last component defines the type and number of surface groups, Z. The DSM generation (G') designation counts the number of iteration steps rather than the branch cell formation stages. Therefore, compared to the literature notation used here, $G' = G - 1$.

PREPARATIVE TECHNIQUES POPAM dendrimers are synthesized by the divergent method starting from 1,4-diaminobutane (DAB) ($N_c = 4$). They are amplified by progressing through a reiterative sequence consisting of (a) a double Michael addition of acrylonitrile to the primary amino groups followed by (b) hydrogenation under pressure in the presence of Raney cobalt. Products are produced up to generation = 4 (literature); generation = 5 (DSM) nomenclature ($Z = 64$).[1]

PROPERTIES OF SPECIAL INTEREST Unique dendrimer properties not found in traditional macromolecular architecture include: (1) a distinct parabolic intrinsic viscosity curve with a maximum as a function of molecular weight; (2) very monodispersed sizes and shapes (i.e., $\overline{M}_w/\overline{M}_n$ routinely below 1.1 even at high molecular

weights);[2] (3) *exo* presentation of exponentially larger numbers of surface functional groups as a function of generation (i.e., up to several thousand); and (4) typical Newtonian-type rheology. This dendrimer family exhibits excellent hydrolytic and thermal stability.

MAJOR APPLICATIONS Used as templates for initiation of caprolactam polymerization to produce injection moldable star-like-Nylon-6 products.[3] This dendrimer family has been used in a variety of metal chelation, coatings, and lubrication-type applictions.[4]

SUPPLIER DSM, Het Overloon 1, Heerlen, P.O. Box 6500, 6401 JH Heelen, The Netherlands.

Data for amine terminated polypropylenimine dendrimer DAB-*dendri*-$(NH_2)_x$

Generation		DSM designation	Molecular weight (g mol^{-1})*	Number of surface groups	[η]25°C D_2O (dl g^{-1})	V_η (Å^3)	R_η (Å)	R_g(SANS) (D_2O) (Å)	Modeling (Å)	
Literature	DSM								R_g(cvff)	R_g(cvffrep)
0	1	DAB-*dendri*-$(NH_2)_4$	317	4	0.045	948	6.1	4.4	4.9	5.0
1	2	DAB-*dendri*-$(NH_2)_8$	773	8	0.055	2,824	8.8	6.9	6.0	7.6
2	3	DAB-*dendri*-$(NH_2)_{16}$	1,687	16	0.062	6,947	11.8	9.3	7.4	10.1
3	4	DAB-*dendri*-$(NH_2)_{32}$	3,514	32	0.068	15,872	15.6	11.6	10.0	12.9
4	5	DAB-*dendri*-$(NH_2)_{64}$	7,168	64	0.068	32,367	19.8	13.9	12.5	15.9

* Theoretical values.

Data for nitrile terminated polypropylenimine dendrimer DAB-*dendri*-(CN)x

Generation		DSM designation	Molecular weight (g mol^{-1})*	Number of surface groups	[η]$^{25°C}$ (acetone) (dl g^{-1})	V_η (Å^3)	R_η (Å)	R_g(SANS) (acetone-d_6) (Å)
Literature	DSM							
0	1	DAB-*dendri*-$(CN)_4$	300	4	0.024	478	4.9	–
1	2	DAB-*dendri*-$(CN)_8$	741	8	0.030	1,477	7.1	6.0
2	3	DAB-*dendri*-$(CN)_{16}$	1,622	16	0.034	3,663	9.6	8.0
3	4	DAB-*dendri*-$(CN)_{32}$	3,385	32	0.035	7,869	12.3	10.1
4	5	DAB-*dendri*-$(CN)_{64}$	6,910	64	0.036	16,523	15.8	12.2

*Theoretical values.

DSM DESIGNATION	UNITS	DAB/ACN4	DAB/ACN8	DAB/ACN16	DAB/ACN32	DAB/ACN64
Generation	–					
DSM		1	2	3	4	5
Literature		0	1	2	3	4
End groups	–	4*CN	8*CN	16*CN	32*CN	64*CN
Molecular weight	g mol^{-1}	300	741	1,622	3,385	6,910
Diameter	nm	1.4	1.9	2.6	3.3	4.3
Radius of gyration (acetone-d_4)	Å	–	6	8	10.1	12.2
Density	g cm^{-3}	–	1.0600	1.0582	–	–
Appearance	–	White powder	Sl. yellow vis. liq.	–	–	–
Melting point	K	326	–	–	–	–
Viscosity, bij 50°C	Pa s	–	2.6	10.3	15	50
Intrinsic viscosity	d g^{-1}					
25°C/acetone		0.026	0.031	0.035	0.038	0.038
25°C/THF		−0.028	−0.034	−0.042	−0.045	−0.045
T_g onset	K	213.5	218.8	225.8	227.8	232.9

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DSM DESIGNATION	UNITS	DAB/ACN4	DAB/ACN8	DAB/ACN16	DAB/ACN32	DAB/ACN64
T_gA maximum, 20°C min^{-1}	K	603	603	603	603	603
Thermal stability	K	483	483	483	483	483
Vapor pressure	–	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Safety data						
Flash point	K	375	442	–	–	–
Autoignition	K	692	658	–	–	–
Ames test	–	Not carcinogen	Not carcinogen	Not carcinogen	Not carcinogen	Not carcinogen
Irritation	–	Mild irritating	–	Not irritating	–	–
Labeling by irritation	–	None	–	None	–	–
LD50 test	mg kg^{-1}	>5,000	–	–	4,000	–
Labeling by LD50 test	–	None	–	–	None	–

DSM DESIGNATION	UNITS	DAB/PA4	DAB/PA8	DAB/PA16	DAB/PA32	DAB/PA64
Generation	–					
DSM		1	2	3	4	5
Literature		0	1	2	3	4
End groups	–	4*NH_2	8*NH_2	16*NH_2	32*NH_2	64*NH_2
Molecular weight	g mol^{-1}	317	773	1,687	3,514	7,166
Diameter	nm	1.5	1.9	2.7	3.4	4.4
Radius of gyration (D_2O)	Å	4.4	6.9	9.3	11.6	13.9
Density	g cm^{-3}	0.9578	0.9785	0.989	1.0097	
Appearance	–	Light yellow oil	Light yellow oil	Light yellow oil	Light yellow oil	Light yellow oil
Melting point	K	~298	–	–	–	–
Viscosity, bij 50°C	Pa s	0.028	0.28	1.1	2.5	6.7
Intrinsic viscosity						
25°C/D2O	d g^{-1}	0.045	0.055	0.062	0.068	0.068
25°C/THF		0.026	0.036	0.04	–	–
25°C/MeOH		0.046	0.055	0.061	0.064	0.059
T_g onset	K	166	176	183	186	189
T_gA maximum, 20°C min^{-1}	K	~623	~718	~718	~718	~718
Thermal stability	K	tot 573	tot 573	>573	>573	>573
Vapor pressure	–	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Safety Data						
Flash point	K	406	–	–	–	–
Autoignition	K	597	–	–	–	–
Ames test	–	Not carcinogen	Not carcinogen	Not carcinogen	Not carcinogen	Not carcinogen
Irritation	–	Strong	–	Strong	Strong	–
Labeling by irritation	–	Corrosion, R41	–	Corrosion, R41	Corrosion, R41	–
LD50 test	mg kg^{-1}	977	–	1,373	–	–
Labeling by LD50 test	–	Harmful	–	Harmful	–	–

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Poly(trimethylene oxide)

QINGWEN WENDY YUAN

ACRONYM PTMO

CLASS Polyethers

STRUCTURE $[-CH_2-CH_2-CH_2-O-]$

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	58		–
Polymerization	–	–	Ring-opening		(1)
Theta temperature	K	Cyclohexane, phase equilibria	299.5		(2, 3)
Mark-Houwink parameter: K and a	$K = ml\,g^{-1}$ a = None		K ($\times 10^{-3}$)	a	(2, 4)
		Acetone, 30°C, (2.8–20) $\times 10^4$ $g\,mol^{-1}$	76	0.59	
		Benzene, 30°C, (2.8–30) $\times 10^4$ $g\,mol^{-1}$	21.9	0.78	
		Carbon tetrachloride, 30°C, (2.8–25) $\times 10^{-4}$ $g\,mol^{-1}$	26.7	0.75	
Solubility parameter	$(MPa)^{1/2}$	Method: viscosity, 25°C	19.2		(2, 5)
Glass transition temperature	K	–	195		(2, 6–8)
Melting temperature	K	–	308		(2)
Heat capacity	$kJ\,K^{-1}\,mol^{-1}$ ($\times 10^{-3}$)	Temp. (K)	Solid	Melt	(2, 9)
		10	0.86	–	
		20	4.68	–	
		30	9.31	–	
		40	13.65	–	
		50	17.64	–	
		60	21.37	–	
		70	25.82	–	
		80	29.59	–	
		90	32.90	–	
		100	35.87	–	
		110	38.58	–	
		120	41.11	–	
		130	43.51	–	
		140	45.83	–	
		150	48.11	–	

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Poly(trimethylene oxide)

PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Heat capacity	kJ K^{-1} mol^{-1} ($\times 10^{-3}$)	Temp. (K)	Solid	Melt	(2, 9)
		160	50.37	–	
		170	52.65	–	
		180	54.97	–	
		190	57.33	–	
		200	59.01	109.24	
		210	61.08	110.25	
		220	63.15	111.26	
		230	65.23	112.27	
		240	67.30	113.28	
		250	69.37	114.29	
		260	71.44	115.30	
		270	73.51	116.31	
		280	75.59	117.32	
		290	77.66	118.33	
		300	79.73	119.34	
		310		120.35	
		320		121.36	
		330		122.37	
Specific refractive index increment dn/dc	ml g^{-1}	Solvent: MEK	0.0946		(2, 10)
Fractionation	–	Fractional precipitation	Acetone/water		(2)

Crystalline-state properties[2]

Lattice	Space group	Unit cell parameters (Å)			Angles (degrees)	Monomers per unit cell	Density (g cm^{-3})
		a	*b*	*c*			
Monoclinic	C2H-3	12.3	7.27	4.80	$\beta = 91$	4	1.178
Rhombohedral	C3V-6	14.13	14.13	8.41	–	18	1.941
Orthohombic	D2-5	9.23	4.82	7.21	–	4	1.203
				4.79	–	–	–

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Poly[1-(trimethylsilyl)-1-propyne]

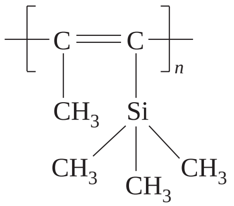
TAREK M. MADKOUR

ACRONYM PTMSP

CLASS Conjugated and other unsaturated polymers

SYNTHESIS Polyaddition

STRUCTURE



MAJOR APPLICATIONS Potential applications involve oxygen enrichment applicable to combustion furnaces, car engines, and respiration-aiding apparatuses. Also in the transport of oxygen dissolved in water applied to contact lenses and artificial lungs. In liquid mixture separation associated with ethanol concentration of fermented biomass. Furthermore, in polymer degradation related to resist materials for microlithography.

PROPERTIES OF SPECIAL INTEREST Glassy ductile polymer with high permeability and low selectivity. A white amorphous silicon containing acetylene stable to air and soluble in nonpolar solvents such as toluene, cyclohexane, and carbon tetrachloride. Thus, it allows for tough film formation by solution casting.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	112.25	(1)
Typical molecular weight range	$g\,mol^{-1}$	–	1.3–6.1 ($\times 10^5$)	(1)
Typical polydispersity range (M_w/M_n)	–	–	1.4–2.4	(1)
Characteristic infrared bands	cm^{-1}	Group assignments		(2)
		SiC–H deformation	1,240	
		C–Si stretching	820, 740	
UV absorption maximum (λ_{max})	cm ($\times 10^7$)	–	273	(3)
UV molar extinction coefficient (ε_{max})	$mol^{-1}\,cm^{-1}$	–	120	(3, 4)
Density	$g\,cm^{-3}$	Measured at 21°C	0.964	(5)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Geometric density	$g\,cm^{-3}$	Geometric density refers to that of thin membranes (usually of lower value than real density)	0.7–0.77	(5)
Mark-Houwink parameter: K and a	$K = ml\,g^{-1}$ a = None	–	4.45×10^{6} $a = 1.04$	(3)
Glass transition temperature	K	–	503	(6)
Softening point	K	–	613	(3)
Young's modulus	MPa	–	630	(3)
Tensile strength	MPa	–	40	(3)
Elongation at break	%	–	73	(3)
Electrical conductivity	$s\,cm^{-1}$	–	1×10^{-17}	(1)
Permeability coefficients	m^3 (STP) m s^{-1} m^{-2} Pa^{-1}	Gas (at 25°C)		(7)
		He	4.65×10^{-14}	
		H_2	1.24×10^{-13}	
		O_2	6.6×10^{-14}	
		N_2	4.8×10^{-14}	
		CO_2	2.64×10^{-13}	
		CH_4	1.27×10^{-13}	
Diffusion coefficients	$m^2\,s^{-1}$ $(\times 10^{12})$	Gas (at 25°C)		(7)
		N_2	3,600	
		Ar	3,900	
		CH_4	3,200	
		CO_2	3,000	

Dual-mode parameters[7]

Gas (at 25°C)	Sorption parameters			Diffusion coefficients	
	k_D [m^3 (STP) m^{-3} atm^{-1}]	C'_H [m^3 (STP) m^{-3}]	b (atm^{-1})	$D_D \times 10^9$ ($m^2\,s^{-1}$)	$D_H \times 10^9$ ($m^2\,s^{-1}$)
CO_2	1.0667	111.7	0.0688	16.2	1.95
CH_4	0.6328	58.87	0.0577	–	–
Ar	0.8313	24.23	0.0325	–	–
N_2	0.7103	16.10	0.0394	5.23	3.46

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Void volume fraction	—	Gas/Temp. (°C)		(7)
		N_2/−195	0.26	
		CO_2/25	0.24	
		SF_6/25	0.23	
Interchain gap	Å	—	3.3	(7)
Intrinsic viscosity [η]	dl g^{-1}	Polymerized at 80°C and measured in toluene at 30°C		(1)
		Catalyst		
		$NbCl_5$	0.99	
		$NbBr_5$	0.63	
		$TaCl_5$	5.43	
		$TaBr_5$	3.60	
Time required for 2% weight loss	min	TGA measurement in air		(8)
		145°C	860	
		161°C	430	
		176°C	225	
		186°C	100	
		198°C	76	
		206°C	51	

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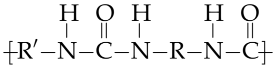
Polyurea

L. S. RAMANATHAN, S. SIVARAM, AND MUNMAYA K. MISHRA

ACRONYMS PU, PUR

CLASS Polyureas

STRUCTURE



R = isocyanate unit
R′ = diamine unit

MAJOR APPLICATIONS The most important practical applications of polyurea elastomers are in the production of automobile parts. High-modulus RIM (reaction-injection molded) and RRIM (reinforced reaction-injection molded) polyureas are suitable for producing high-impact external body panels. It is also useful in the forming microporous films for artificial leather. Ultrathin membranes of polyurea are used in water desalination by reverse osmosis. Polyureas are effective in making lubricant greases, medical equipment and artificial organs. Polyurea is also applied as a wall material for encapsulating drugs, pesticides, catalysts, and other products.

PROPERTIES OF SPECIAL INTEREST Polyurea fibres have high melting points, low specific gravity, excellent dyeability, and good acid and alkaline resistance. Polyurea coatings have lower solvent and better water resistance compared to polyurethanes. They have good blood compatibility.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	1,9-Nonane diamine (NDA)/ethylene bis chloroformate (EBC)	1.175	(1)
		1,10-Decane diamine (DDA)/EBC	1.75	(1)
		Polyisocyanate/polyetheramine/diethyl toluene diamine (DETDA)	1.1	(2)
		Aliphatic-aromatic copolyureas	1.012–1.214	(3)

Unit cell dimensions

Sample	Lattice	Cell dimensions (Å)			Cell angles (degrees)			Reference
		a	*b*	*c*	α	β	γ	
4,4′-Dicyclohexyl methane diisocyanate (CHMDI)/1,10 DDA	—	9.30	6.06	45	—	—	—	(4)
4,4′-diphenyl methane diisocyanate (MDI)/1,4-butane diamine (BDA)	Triclinic	4.63	5.83	25.23	90.7	91.58	102.9	(5)

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Refractive indices of polyurea before poling[6]

System	Wavelength (μm)	RI	
		^{n}TE	^{n}TM
MDI/4,4′-methylene bis(cyclohexyl amine)	0.532	1.6052	1.5834
	0.6328	1.5962	1.5761
	1.064	1.5762	1.5644
MDI/1,4-diaminocyclohexane	0.532	1.6152	1.6012
	0.6328	1.6089	1.5949
	1.064	1.5838	1.5762
MDI/2,2-dimethyl-1,3-propane diamine	0.532	1.6223	1.6127
	0.6328	1.6091	1.5995
	1.064	1.5919	1.5833
MDI/4,4′-diaminodimethyl sulfone	0.532	1.7088	1.6715
	0.6328	1.6872	1.6564
	1.064	1.6577	1.6340

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Piezoelectric '*e*' constant	$mC\,m^{-2}$	MDI/4,4′-diaminodiphenylmethane (MDA)	15	(7)
Heat capacity	—	MDI/polyether amine/DETDA	0.41	(8)
Glass transition temperature	K	1,9-NDA/EBC	277	(1)
		1,10-DDA/EBC	333.8	(1)
		Octafluoro hexamethylene-1,6-diamine (OFHMDA)/1,6-hexamethylene bis(chlorocarbonate) [HMCC]	278	(9)
		Hexamethylene diamine (HMDA)/HMCC	271	(9)
		MDI/polyether amine/DETDA	215	(10)
		Amino terminated polysilanes/MDI/DETDA	186	(11)
		Amino terminated polysilanes/MDI+HMDI/1,3-propane sulfonate	180	(11)
		Amino terminated polysilanes/MDI+HMDI/ethylene diamine (EDA)	176	(11)
Melting temperature	K	4,4′-methylenebis[N-methyl aniline]/2,2-dimethyl-1,3-propanediol bis(chloroformate)	443–463	(12)
		4,4′-methylenebis[N-methyl aniline]/$COCl_2$	523–553	(12)
		$ClCON(CH_3)C_6H_4CH_2C_6H_4N(CH_3)COCl$/$HN(CH_3)(CH_2)_6(CH_3)NH$	383–453	(12)
		4,4′-diamino-1,3-diphynyl propane/EBC	480	(1)
		4,4′-diamino-1,3-diphynyl butane/EBC	547	(1)
		1,9-NDA/EBC	441	(1)
		1,10-DDA/EBC	447	(1)
		OFHMDA/HMCC	457	(9)
		HMDA/HMCC	443	(9)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Water absorption	%	MDI based polyurea at 25°C, 7 days	2.13	—
Solubility parameter	$(MPa)^{1/2}$	MDI/EDA	24.9	(13)
		MDI/DETDA	23.9	
		MDI/methylene bis(2,6-isopropyl aniline) (MMIPA)	21.6	
		MDI/methylene bis(2-methyl-6-isopropyl aniline) [MDIPA]	20.4	
Tensile strength	MPa	Aminopropyl terminated poly(dimethyl siloxane) [ATPDMS]/MDI	16.6	(14)
		ATPDMS/TDI	10.0	(14)
		ATPDMS/HMDI	9.0	(14)
		MDI/polyether amine/DETDA	4.61	(10)
		MDI/polyether amine/DETDA	15.9	(8)
		Amino terminated polysilanes/MDI/DETDA	9.1	(11)
		Amino terminated polysilanes/MDI+HMDI/ 1,3-propane sulfonate	22.4	(11)
		Amino terminated polysilanes/MDI+HMDI/ED	16.1	(11)
Elongation	%	ATPDMS/MDI	430	(14)
		ATPDMS/TDI	520	(14)
		ATPDMS/HMDI	950	(14)
		MDI/polyether amine/DETDA	276	(8)
		MDI/ polyether amine/DETDA	250	(10)
		Amino terminated polysilanes/MDI/DETDA	426	(11)
		Amino terminated polysilanes/MDI+HMDI/ 1,3-propane sulfonate	335	(11)
		Amino terminated polysilanes/MDI+HMDI/EDA	332	(11)
Shore D hardness		Polyisocyanate/polyether amine/DETDA	75	(2)
Tear strength	$N\ m^{-1}$	IPDI based polyurea	70×10^3	(15)
		Tetramethyl xylene diisocyanate (TMXDI) based polyurea	45×10^3	

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Polyurethane

L. S. RAMANATHAN, S. SIVARAM, AND MUNMAYA K. MISHRA

ACRONYMS PU, PUR

CLASS Polyurethanes

STRUCTURE

$$-O\!\left[\left(R'\right)_x O-\overset{\overset{O}{\|}}{C}-NH-R-NH-\overset{\overset{O}{\|}}{C}-O\right]_n$$

R = isocyanate unit
R′ = polyol segment

MAJOR APPLICATIONS Polyurethane flexible foams find applications in protective packaging, gaskets, textile laminates, protective cushioning in automobiles, and two component injection-grouting resins. Rigid polyurethane foams are used as thermal insulating materials in refrigerators, freezers, and water heaters. It is also used as a roof proofing material.

PROPERTIES OF SPECIAL INTEREST Excellent dampening property, good mechanical and physical properties even at low temperatures, high combustion resistance, and low thermal conductivity.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	4,4′-Diphenylmethane diisocyanate (MDI)/1,4-butane diol (BD)	1.297	(1)
Flory-Huggins polymer solvent interaction parameter	—	TDI/1,4-BD (DMF)	0.122	(2)

Unit cell dimensions

Sample	Lattice	Cell dimensions (Å)			Cell angles (degrees)			Reference
		a	*b*	*c*	α	β	γ	
Hexamethylene diisocyanate (HMDI)/ Ethylene glycol (EG)	Triclinic	4.59	5.14	13.9	90	90	119	(3)
HMDI/1,3-propane diol (PD)	Monoclinic	4.70	8.36	33.9	—	—	115	(3)
HMDI/BD	Triclinic	4.98	4.71	19.4	116	105	109	(3)
HMDI/1,5-pentane diol (PtD)	Monoclinic	4.70	8.36	39.0	—	—	115	(3)
HMDI/1,6-hexane diol (HD)	Triclinic	5.05	4.54	21.9	112	108	108	(3)
Trimethylene diisocyanate (TMDI)/BD	Triclinic	5.06	5.04	30.1	112	113	110	(4)
TMDI/HD	Triclinic	5.04	5.04	34.6	111	111	111	(4)
MDI/BD	Triclinic	5.2	4.8	35	115	121	85	(5, 6)
MDI/BD	Triclinic	4.92	5.66	38.4	124	104	86	(7)

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Conformational characteristics

Sample	Solvent	Mark-Houwinck parameters		$[\langle R^2\rangle/M]^{1/2}\times 10^9$	Reference
		$K\times 10^{-4}$ (ml g^{-1})	a		
Toluene diisocyanate (TDI)/BD	–	5.4	0.74	–	(2)
MDI/EG	100 DMF	3.64	0.71	10.11	(8)
	95/5 DMF/acetone	6.29	0.65	10.19	(8)
	90/10 DMF/acetone	7.19	0.63	10.25	(8)
	85/15 DMF/acetone	10.02	0.59	10.04	(8)
	79/21 DMF/acetone	14.19	0.56	9.97	(8)
	71/29 DMF/acetone	30	0.50	–	(8)
MDI/BD	DMA (at 25°C)	870	1.43	–	(9)

Refractive index gradient

Sample	Condition			dn/dc (ml g^{-1})	Second virial coefficient $A_2\times 10^4$	Reference
	Solvent	λ (nm)	Temp (°C)			
TDI/BD	DMF	546	–	0.14	–	(2)
MDI/1,6-HD	DMF/acetone	–	–	0.159–0.203*	3.0–4.5*	(10)
	DMF/toluene	–	–	0.123–0.154*	2.3–8.0*	(10)

*Variable with respect to DMF volume fraction.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of fusion	kJ mol^{-1}	MDI/BD	5.3	(9)
Heat capacity	cal g^{-1} °C^{-1}	HMDI/BD		(11)
		−50 to 10°C	0.422	
		45–120°C	0.495	
		195–210°C	0.665	
		HMDI/DEG		
		−50 to −5°C	0.422	
		50–100°C	0.512	
		140–160°C	0.623	
Crystallization half time	min	HMDI/BD	6	(12)
		HMDI/diethylene glycol (DEG)	10.5	
Crystallization enthalpy	cal cm^{-3}	HMDI/BD	40	(12)
		HMDI/DEG	45	
Glass transition temperature	K	HMDI/BD	295	(12)
		HMDI/DEG	272	(12)
		HMDI/octafluoro1,6-hexane diol (OFHD)	271	(13)
		MDI/EG	363	(14)
		Desmodur/1,6-HD	322	(15)
		Desmodur/cyclohexane dimethanol (CHDM)	302	(15)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melting temperature	K	HMDI/BD	476	(12)
		HMDI/DEG	396	(12)
		HMDI/OFHD	399	(13)
		TDI/EG	453	(14)
		MDI/EG	498	(14)

Optical properties

System	Temp. (°C)	Solvent	Optical rotation $[\infty]_D$	Reference
MDI/(1S,2S)-diphenyl propane diol	25	DMSO	−71.6	(16)
HMDI/(1S,2S)-diphenyl propane diol	25	DMSO	−14.7	(16)
HMDI/(2R,4R)-pentanediol	25	DMSO	−80.6	(16)
MDI/(1S,2S)-(+)-2-acetamido-1-phenyl-1,3-propanediol	25	DMF	−24.6	(17)
TDI/(1S,2S)-(+)-2-acetamido-1-phenyl-1,3-propanediol	25	DMF	−20.6	(17)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Photoconductivity	$ohms^{-1}\ cm^{-1}$	Polyurethane with pendant chromophore	1.3×10^{-13}	(18)
Refractive index	—	Polyurethane with pendant chromophore		(18)
		At 532 nm	1.879	
		At 690 nm	1.812	
		At 1,064 nm	1.763	
Water vapor absorption	%	MDI/EG	2.5	(14)
Solubility parameter	$(MPa)^{1/2}$	MDI/BD	27	(1)
		MDI/EG	21	(19)
Elongation	%	MDI/EG	36	(14)
Adhesion strength	psi	Desmodur/1,6-HD	220	(15)
		Desmodur/CHDM	220	

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Polyurethane elastomers

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ACRONYMS PU, PUR

CLASS Polyurethanes

STRUCTURE

$$\left[\!-(R'')_x\!-O-\right]\left[-\overset{\displaystyle O}{\overset{\|}{C}}-NH-R-NH-\overset{\displaystyle O}{\overset{\|}{C}}-O-(R')_y-\right]_n\!-O-$$

R = isocyanate unit
R′ = polyol segment
R″ = diol segment

MAJOR APPLICATIONS Polyurethane elastomers find applications in adhesives, laminates for textiles, covering of conveyor and drive belts, welded bodies, roof underlay sheeting, magnetic tape coatings, water line tubing, and ski boot manufacture. Elastomeric RIM polyurethanes are useful in making automotive parts such as bumpers and fascia. Reinforced RIM polyurethane has been used for car windows door panels and wind shields. Foamed elastomeric polyurethanes are also used in making automotive parts such as arm rests, steering wheels, and rear deck air domes.

PROPERTIES OF SPECIAL INTEREST Excellent toughness and wear resistance with a broad temperature range for use. Polyurethane has good blood and tissue compatibility.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	Oxyester/toluene diisocyanate (TDI)/1,4-butane diol(BD)	1.240	(1)
		Oxyester/4,4′-diphenylmethane diisocyanate (MDI)/BD	1.213	(1)
		Oxyester/hexamethylene diisocyanate (HDI)/BD	1.163	(1)
		Oxyester/Isophorone diisocyanate (IPDI)/BD	1.160	(1)
		Poly(oxyethylene) (PEO) diol/MDI/BD	0.986	(2)
		Poly(tetramethyleneoxide) PTMO/MDI/BD	1.004	(2)
		Poly(propyleneoxide) PPO/MDI/BD	0.976	(2)

Unit cell dimensions

Sample	Lattice	Cell dimensions (Å)			Cell angles (degrees)			Reference
		a	*b*	*c*	α	β	γ	
PTMO/MDI/BD	Triclinic	5.05	4.67	37.9	116	116	83.5	(3)
PTMO/MDI/Hexane diol (HD)	Triclinic	4.99	—	41.5	114.5	113.8	84.3	(4)
Poly(tetramethyleneadipate) [PTMA]/MDI/HD	Triclinic	5.1	5.1	41.6	116	116	85	(5)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Flory-Huggins interaction parameter	—	PE0/MDI/BD	−0.27	(2)
		PTMO/MDI/BD	−0.33	
		PPO/MDI/BD	−0.08	
Flory-Huggins polymer solvent interaction parameter	—	Chloroform	0.228	(6)
		Benzene	0.333	
		MEK	0.417	
		Dibutyl ether	0.521	
		Acetonitrile	0.606	
		Cyclohexane	0.660	

Conformational characteristics[7]

Sample	Mark-Houwink parameters		K_0	$\overline{R}_0^2$
	K (ml g^{-1})	a	(g$^{-3/2}$ mol$^{1/2}$ cm^3)	(Å^2 mol g^{-1})
Poly (caprolactone) diol (PCL)/MDI/BD	0.257	0.54	0.25	1.0
PTMA/MDI/BD	0.043	0.70	0.20	0.84

Refractive index gradient[7,8]

Sample	Conditions			dn/dc (ml g^{-1})
	Solvent	λ (nm)	Temp (°C)	
PCL/MDI/BD	DMF	546	25	0.102
PTMA/MDI/(BD)	DMF	546	25	0.110
TDI/poly (propylene) glycol (PPG)	Benzene	435.8	—	0.031
TDI/PPG	Butanone	435.8	—	0.094
TDI/PPG	Methanol	435.8	—	0.148

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of fusion	kJ mol^{-1}	PEO/MDI/BD	197	(9)
		PEO/MDI/BD	155	
Glass transition temperature	K	PPG/MDI/BD	222	(10)
		PCL/MDI/BD	250	(11)
		Poly(ethyleneadipate)[PEA]/MDI/BD	230	(12)
		Hydroxy terminated poly(butadiene) [HTPB]/TDI/BD	246	(13)
		PTMO/2,4-TDI/BD	208	(14)
		PTMO/2,6-TDI/BD	200	(14)
Melting temperature	K	PCL/MDI/BD	358; 426	(11)
		PPG/MDI/BD	462; 468	(10)
		PTMG/poly (dimethylsiloxane) [PDMS]/MDI/EG	505	(15)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric loss	–	PEA/MDI	0.8	(16)
		PPO/MDI/BD (at 12.5C)	2.2	(9)
Bulk DC conductivity	$ohm^{-1} cm^{-1}$	PPO/MDI/BD (at 12.5°C)	22×10^{12}	(9)
Surface resistivity	ohm	Oxyester/MDI/BD	1.8×10^{12}	(1)
Volume resistivity	ohm cm	Oxyester/MDI/BD	6.9×10^{11}	(1)
Contact angle	degrees	Water	89	(17)
		Water/propanol	69	
		α-Br napthalein	25	
Surface free energy	$erg\,cm^{-2}$	Estane 5714 FI (BF Goodrich)	21	(17)
Permeation rate	$mg\,cm^{-1}\,day^{-1}$	At 25°C		(18)
		Water	0.33	
		LiCl	0.27	
		NaCl	0.24	
		KCl	0.32	
		CsCl	0.28	
Solubility parameter	$(MPa)^{1/2}$	PPG(1000)/MDI/BD	23	(10)
		PPG(2000)/MDI/BD	23	
		PPG(3000)/MDI/BD	23	
Loss factor tan δ	–	PTMO/MDI/BD	0.072	(19)
Activation energy	$kJ\,mol^{-1}$	PEA/MDI/BD	152.5	(16)
		PTMO/MDI/BD	224	(19)
Tensile strength	MPa	PTMO/MDI/BD	45	(18)
		PTMO/MDI/BD (NCO/OH = 2/1)	20.16	(20)
		PTMO/MDI/BD (NCO/OH = 4/1)	37.59	(20)
Elongation	%	PTMO/MDI/BD	850	(21)
		PTMO/MDI/BD (NCO/OH = 2/1)	1,100	(20)
		PTMO/MDI/BD (NCO/OH = 4/1)	649.2	(20)
Shore A hardness	–	Poly(butyleneadipate) [PBA]/MDI/BD	85	(22)
Thermal expansion coefficient	K^{-1}	–	280	(23)

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Polyurethane urea

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ACRONYMS PU, PUU

CLASS Polyurethanes

STRUCTURE

$$-O\left[\left(R'\right)_x O-\overset{\displaystyle O}{\overset{\|}{C}}-NH-R-NH-\overset{\displaystyle O}{\overset{\|}{C}}\right]_n\left[NH-R''\right]_m$$

x = DP of soft segment; R = isocyanate unit
R′ = soft segment; R″ = amine unit

MAJOR APPLICATIONS Polyurethane urea is useful in making interior automobile parts like armrests, head rests, gear shifts, knee protection pad, etc. Rigid integral PU foams are used in electronic and construction fields.

PROPERTIES OF SPECIAL INTEREST High compressive strength, less weight, good weatherability, and excellent properties of electrical insulation.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	g cm^{-3}	4,4′-Diphenylmethane diisocyanate (MDI)/polyether polyol/ 4,4′-diaminodiphenyl methane (MDA)	0.96	(1)
		MDI/polyether polyol/diethyl toluene diamine (DETDA)	0.98	
		MDI/polyether polyol/3-chloro-3′methoxy-4,4′diamino diphenylmethane (CMOMDA)	0.94	

Unit cell dimensions[2]

Sample	Lattice	Cell dimensions (Å)			Cell angles (degrees)		
		a	*b*	*c*	α	β	γ
MDI/poly(tetramethylene oxide) (PTMO)/MDA	Monoclinic	4.72	11.33	11.64	—	—	116.5

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Electron density (mean square fluctuation)	mol electron cm^{-3}	2,4-Toluenediisocyanate (TDI)/PTMO/ ethylenediamine (EDA)	7.14×10^{-3}	(3)
Bragg spacing	Å	2,4-TDI/PTMO/EDA	140	(3)
Flory-Huggins polymer solvent interaction parameter	—	MDI/polycaprolactone diol (PCL) M_n = 1,300/EDA (dimethylacetamide)	0.32	(4)
		MDI/PCL(1,300)/EDA (dimethylformamide)	0.4	
		MDI/PCL(1,300)/EDA (dimethylsulfoxide)	0.45	
		MDI/PCL(2,800)/EDA (dimethylformamide)	0.42	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Partial specific volume	—	At 25°C in DMF MDI/PCL(1300)/EDA	0.848	(4)
		MDI/PCL(2800)/EDA	0.875	
Heat of fusion	$J g^{-1}$	MDI/ polyether polyol /MDA	26.4	(1)
		MDI/polyether polyol/DETDA	11.9	(1)
		MDI/ polyether polyol /CMOMDA	18.6	(1)
		MDI/PTMG/1,2-propylenediamine (PDA)	21.49	(5)
Heat capacity	$J g^{-1} K$	MDI/hydroxy terminated polybutadiene (HTPB)/ 4,4′methyleme bis(2-chloroaniline (MOCA)	0.4	(6)
		MDI/HTPB/1,4-butanediamine (BDA)	0.389	(6)
		IPDI/PTMO/methylene bis(2-methyl-6-ethyl aniline) [MBMEA]	0.44	(7)
		IPDI/PTMO/methylene bis(2-methyl-6-isopropyl aniline) [MMIPA]	0.45	(7)
		Trimethyl hexamethylene diisocyanate/PTMO/ MBMEA	0.513	(7)
Glass transition temperature	K	MDI/polyether polyol/MDA	215.9	(1)
		MDI/polyether polyol /DETDA	220.9	(1)
		MDI/polyether polyol /CMOMDA	232.8	(1)
		MDI/PTMO/EDA	200	(8)
		MDI/PTMO/MDA	199	(8)
		MDI/PTMO/1,6-hexanediamine (HDA)	200	(8)
		TDI/PTMO/EDA	201	(8)
		2,4-TDI/PTMO(1000)/EDA	220	(9)
		2,4-TDI/PTMO(2000)/EDA	199	(9)
		2,4-TDI/PTMO/EDA	199	(3)
		MDI/PTMO/EDA	225	(10)
		MDI/aminopropyl terminated polycyanoethylmethylsiloxane (ATPCEMS)/ 1,4-butanediol (BD)	194.1	(11)
		Lysinediisocyanate (LDI)/PCL/1,4-BDA	220.9	(12)
		1,4-butanediisocyanate (BDI)/PCL/1,4-BDA	216.3	(12)
		1,6-hexanediisocyanate (HDI)/PCL/1,4-BDA	222	(12)
		Tetramethyl xylene diisocyanate (TMXDI)/PCL/ DETDA	221.7	(13)
		TMXDI/HTPB/DETDA	198.8	(13)
Melting temperature	K	MDI/PTMO/EDA	564	(10)
		MDI/PTMG/1,2-PDA	547	(5)
Melting enthalpy	$J g^{-1}$	MDI/PEG(400)/EDA	60	(14)
		MDI/PEG(1500)/EDA	29	
Dielectric loss	—	TMXDI/PCL/DETDA	0.3	(13)
		TMXDI/HTPB/DETDA	0.04	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric permitivity	–	TMXDI/PCL/DETDA	6.8	(13)
		TMXDI/HTPB/DETDA	3.0	
Activation energy	$kJ\,mol^{-1}$	TDI/POLYESTERDIOL/MOCA	42.7	(15)
		TDI/POLYETHERDIOL/MOCA	66.8	
Tensile strength	MPa	MDI/polyetherdiol/MDA	Brittle	(1)
		MDI/polyetherdiol/DETDA	14.3	(1)
		MDI/polyetherdiol/CMOMDA	10	(1)
		MDI/ATPCEMS/BD	6.65	(11)
		LDI/PCL/1,4-BDA	17	(12)
		BDI/PCL/1,4-BDA	29	(12)
		HDI/PCL/1,4-BDA	38	(12)
		MDI/PPO/DETDA	9.33	(16)
		MDI/PBA/DETDA	14.75	(16)
Elongation	%	MDI/polyetherdiol/MDA	–	(1)
		MDI/polyetherdiol/DETDA	194	(1)
		MDI/polyetherdiol/CMOMDA	103	(1)
		MDI/PTMG/1,2-PDA	360	(5)
		MDI/ATPCEMS/1,4-BD	256	(11)
		MDI/PPO/DETDA	150	(16)
		MDI/PBA/DETDA	267	(16)
Shore A hardness	–	LDI/PCL/1,4-BDA	800	(12)
		BDI/PCL/1,4-BDA	1042	
		HDI/PCL/1,4-BDA	1168	
Shore D hardness	–	2,4-TDI/PTMG/dimethylthio-2,4-toluenediamine (DM-2,4-TDA)	45	(17)
		2,4-TDI/PTMG/trimethylthio-*m*-phenylenediamine (TM-m-PDA)	36	
Tearing energy	$kg\,m^2$	LDI/PCL/1,4-BDA	36	(12)
		BDI/PCL/1,4-BDA	161	
		HDI/PCL/1,4-BDA	137	
Resilience	–	2,4-TDI/PTMG/DM-2,4-TDA	46	(17)
		2,4-TDI/PTMG/TM-m-PDA	37	

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Poly(vinyl acetate)

JIANYE WEN

ACRONYM PVAC

CLASS Vinyl polymers

STRUCTURE $[-CH_2-CH(OCOCH_3)-]$

MAJOR APPLICATIONS Adhesive applications in packaging and wood gluing; chewing-gum bases; PVAC emulsions and resins are used as binders in coatings for paper and as textile finishes.

PROPERTIES OF SPECIAL INTEREST Tasteless, odorless, and nontoxic.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Absorption of water	%	20°C for 24–144 h	3–6	(1)
		23°C	4	(2, 3)
		70°C	6	(2, 3)
Coefficient of thermal expansion	10^{-4} K^{-1}	0°C	2.8	(4)
		20°C	2.8	
		40°C	7.13	
		60°C	7.17	
		80°C	7.20	
		100°C	7.23	
Cohesive energy density	$(MJ\,m^{-3})^{1/2}$	–	18.6–19.09	(5)
Compressibility	$bar^{-1} (\times 10^{-5})$	Glassy state, 0°C	2.9	(4, 6)
		Glassy state, 20°C	3.0	(4, 6)
		40°C	5.2	(4, 6)
		60°C	5.7	(4, 6)
		80°C	6.2	(4, 6)
		100°C	6.7	(4, 6)
		120°C	7.1	(7)
Decomposition temperature	K	–	423	(8)
Thermal degradation $T^{1/2}$	K	Temperature at which the polymer looses 50% of its weight if heated in vacuum for 30 min	542	(9)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Degree of crystallinity	%	*Mol. wt., Annealing temp.*		(10)
		2,236, 0.623 (40°C)	0.701 (160°C)	
		4,042, 0.514	0.623	
		5,246, 0.508	0.562	
		7,568, 0.504	0.615	
		16,856, 0.487	0.587	
Density	$g\,cm^{-3}$	0°C	1.196*	(4)
		20°C	1.89*	(4)
		25°C	1.19	(11)
		50°C	1.17	(11)
		120°C	1.11	(11)
		200°C	1.05	(11)
		T_m	1.28	(11)
		35–100°C	$1.2124 - (8.62 \times 10^{-4})T + (0.223 \times 10^{-6})T^2$ 35–100°C	(4)
Dielectric constant	—	2 MHz		(12)
		50°C	3.3	
		150°C	8.3	
Dielectric loss factor Tan δ	—	2 MHz		(12)
		50°C	150	
		120°C	260	
Dielectric strength	$V\,cm^{-1}$	30°C	3.94×10^5	(13)
		60°C	3.07×10^5	
Diffusion coefficients D	$10^{-8}\,cm^2\,s^{-1}$	Vinyl acetate, 25°C	26.8	(14)
		Styrene, 25°C	15.4	
Dipole moment	eSU (per monomer unit)	20°C	2.3×10^{-18}	(15, 16)
		150°C	1.77×10^{-18}	
Emulsion specifications of PVAC	wt%	Solids	48–55	(5)
	cP	Viscosity	200–4,500	
	—	pH	4–6	
	% max	Residual monomer	0.5	
	mm	Particle size	0.1–3.0	
	—	Particle charge	Neutral or negative	
	$g\,cm^{-3}$	Density at 25°C	0.92	
	—	Stability to borax	Stable or unstable	
	—	Mechanical stability	Good or excellent	
Gas solubility	$cm^3(STP)\,cm^{-3}\,bar^{-1}$	25°C		(5)
		N_2	0.02	
		O_2	0.04	
		H_2	0.023	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass-transition temperature T_g	K	–	301–304	(5)
		Atactic, $M_n = 3,922$	296.6	
		Atactic, $M_n = 1.66 \times 10^5$	304.4	
		Isotactic, $M_n = 105$	298.8	
Hardness	Shore units	20°C	80–85	(5)
Heat capacity	$KJ\,K^{-1}\,mol^{-1}$	−193°C	0.0278	(17)
		27°C	0.1017	(17)
		47°C	0.1583	(17)
		97°C	0.1632	(17)
		ΔC_p	0.010	(18)
Heat conductivity	$J\,s^{-1}\,m^{-1}\,K^{-1}$	–	0.159	(5)
Heat distortion point	K	–	323	(5)
Heat of polymerization	$kJ\,mol^{-1}$	–	87.5	(5)
Huggins coefficients k_H	–	Acetone, 25°C	0.37	(19)
		Chlorobenzene, 32°C	0.43	
		Chloroform, 25°C	0.31	
		Methanol, 18°C	0.61	
		Toluene, 25°C	0.55	
		Benzene, 30°C	0.37	
		Dioxane, 25°C	0.29	
Index of refraction n_D	–	20.7°C	1.4669	(5)
		30.8°C	1.4657	
		52.1°C	1.4600	
		80°C	1.4480	
		142°C	1.4317	
Interfacial tension	$mN\,m^{-1}$	20°C		(5)
		With PE	14.5	
		With PDMS	8.4	
		With PIB	9.9	
		With PS	4.2	
Internal pressure	$MJ\,m^{-3}$	0°C	255	(5)
		20°C	284.7	
		28°C	397.8	
		40°C	431.3	
		60°C	418.7	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Interaction parameter χ	–	Acetone, 30–50°C	0.31–0.39	(20)
		Acetone, 100–140°C	0.32–0.21	(20)
		Benzene, 20°C	0.42	(21)
		Benzene, 30–50°C	0.30–0.26	(20)
		Benzene, 80–140°C	0.44–0.25	(20)
		n-Butane, 100°C	1.97	(20)
		Butanone, 25°C	0.44	(21)
		Chloroform, 80–135°C	−0.17 to −0.09	(20)
		Cyclohexane, 100°C	1.18	(20)
		Ethanol, 100°C	0.80	(20)
		n-Hexane, 100–120°C	2.06–1.71	(20)
		n-Octane, 90–120°C	2.3–1.94	(20)
		1-Propanol, 30–50°C	1.3–1.0	(20)
		Vinyl acetate, 30°C	0.41–0.22	(20)
		Water, 40°C	2.5	(20)

* Glassy state.

Mark-Houwink parameters: *K* and *a*

Solvent	Temp. (°C)	Mol. wt. range ($M \times 10^{-4}$)	$K \times 10^3$ (ml g^{-1})	*a*	Reference
Acetone	20	–72	15.8	0.69	(22)
	25	–1.3	14.6	0.72	(23)
	–	–	21.4	0.68	(21)
	30	–68	17.4	0.70	(24)
	46	–34	13.8	0.71	(25)
Acetonitrile	25	–215	16.2	0.71	(26)
	30	–153	41.5	0.62	(27)
Benzene	30	–86	56.3	0.62	(28, 29)
	35	–40	21.6	0.675	(30)
Butanone	25	–346	13.4	0.71	(31)
	25	–120	42	0.62	(32)
	30	–120	10.7	0.71	(33)
Chlorobenzene	25	–7	110	0.50	(34)
	53	–34	53.7	0.60	(35)
Chloroform	20	–68	15.8	0.74	(24)
	25	–34	20.3	0.72	(35)
	53	–34	14.7	0.74	(35)
Dioxane	25	–34	11.4	0.74	(36)
Ethanol	56.9 (q)	–150	90	0.50	(25)
Methanol	6	–150	–	10.1	(37, 38)
	25	–22	38.0	0.59	(36)
	30	–120	31.4	0.60	(39)
MEK	25	–	15.4	0.71	(21)
Tetrahydrofuran	25	–50	16	0.70	(40)
	35	–117	15.6	0.708	(41)
Toluene	25	–15	108	0.53	(36)
	67	–15	156	0.49	(36)

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Poly(vinyl acetate)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Modulus of elasticity	MPa	–	$1.275–2.256 \times 10^3$	(5)
Notched impact strength	$J\,m^{-1}$	–	102.4	(5)
Elongation at break	%	20°C, % RH	10–20	(5)
Rubbery shear modulus	$N\,mm^{-2}$	–	13	(5)
Tensile strength	MPa	–	29.4–49.0	(5)
Young's modulus	MPa	–	600	(5)
Melting temperature T_m	K	–	448	(11)
Molar volume	$cm^3\,mol^{-1}$	25°C	74.25	(5)

Permeability and diffusion coefficients

Permeant	Temp. (°C)	$P \times 10^{13}$ *	$D \times 10^6$ *	$S \times 10^6$ *	Reference
He	10	4.95	6.46	0.0784	(42)
	30	9.44	9.55	0.101	(42)
H_2	10	2.99	1.32	0.237	(42)
	30	6.84	2.63	0.254	(42)
Ne	10	0.838	0.794	0.106	(42)
	30	1.97	1.66	0.118	(42)
O2	10	0.136	0.0178	0.766	(42)
	30	0.367	0.0562	0.637	(42)
	73	0.27	–	–	(5)
Ar	10	0.0569	0.00479	1.11	(42)
	30	0.143	0.0162	0.943	(42)
Kr	10	0.0172	0.000602	2.78	(43)
	30	0.0582	0.00295	1.96	(43)
CH_4	25	0.0237	0.0017	1.39	(43)
N_2, below T_g	–	0.066	–	–	(5)
N_2, above T_g	–	0.05	–	–	(5)

*Units are: P in $cm^3(273.15\,K; 1.013 \times 10^5\,Pa)\,cm\,cm^{-2}\,s^{-1}\,Pa^{-1}$; D in $cm^2\,s^{-1}$; S in $cm^3(273.15\,K; 1.013 \times 10^5\,Pa)\,cm^{-2}\,Pa^{-1}$.

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Softening temperature	K	–	308–323	(5)
Specific volume	$L\ kg^{-1}$	$T = 100–200°C$	$0.823 + (6.4 \times 10^{-4})t$	(5)
		$T = 28°C$ (T_g)	0.84	
Solubility parameter	$(MPa)^{1/2}$	–	18.6–19.9	(5)
		25°C	21.07	
		50°C	19.4	
		125°C	17.9	
		∂_d, dispersion forces contribution	19.0	
		∂_p, polar forces contribution	10.2	
		∂_h, hydrogen bonding contribution	8.2	
		∂, $(\partial_d^2 = \partial_p^2 + \partial_h^2)^{1/2}$	23.1	
Surface resistance	$\Omega\ cm^{-1}$	–	5×10^{11}	(5)
Surface tension	$mN\ m^{-1}$	20°C	36.5	(44, 45)
		140°C	28.6	
		150°C	27.9	
		180°C	25.9	
		d_{ds}, dispersive	27.4	
		γ_{os}, polar	15.4	
		γ_{solid}, total	42.85	
	$mN\ m^{-1}\ K^{-1}$	$-d\gamma/dT$	0.066	
	χ^p	Polarity	0.329	
Thermal conductivity	$W\ m^{-1}\ K^{-1}$	–	0.159	(5)
Second virial coefficient A_2	$10^4\ (mol\ cm^3\ g^{-2})$	Acetone, 25°C, $M \times 10^{-4} = 13.71$	6.957	(21)
		Acetone, 30°C, $M \times 10 - 3 = 27–845$	8.80–3.34	(46)
		Acetone, 30°C, $M \times 10^{-3} = 343–722$	3.66–3.50	(47)
		Acetone, 30°C, $M \times 10^{-3} = 78–660$	6.5–2.5	(48)
		Methanol, 25°C, $M \times 10^{-3} = 2{,}360–422{,}900$	7.50–0.172	(49)
Theta solvent	°C	Acetone/isopropanol (23/77)	30	(50)
		Butanone/isopropanol (73.2/26.8)	25	(51)
		Cetyl alcohol	123	(52)
		Di-*i*-butyl ketone	136.5	(53)
		Ethanol	19	(54)
		Ethanol/methanol (80/20)	17	(55)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Theta solvent	°C	Ethanol/methanol (60/40)	26.5	(55)
		Ethanol/methanol (50/50)	34	(50)
		Ethanol/methanol (40/60)	36	(55)
		Heptanone	29	(56)
		Methanol	6	(55)

Unperturbed dimension

Conditions	$r_o/M^{1/2} \times 10^4$ (nm)	$r_{of}/M^{1/2} \times 10^4$ (nm)	$\sigma = r_o/r_{of}$	$C_\infty = r_o^2/nl^2$	Reference
3-Heptanone, 26.8°C	670	332	2.02	8.15	(57)
Methanol, 6°C	720	332	2.17	9.4	(57)
Ethanol, 56.9°C	690	332	2.08	8.65	(57)
Tetrahydrofuran, 35°C	774 ± 20	—	—	—	(58)

PROPERTY	VALUE	REFERENCE
Solvents	Esters, ketones, aromatics, halogenated hydrocarbons, carboxylic acids, alcohols, benzene, toluene, chlorform, carbon tetrachloride/ethanol, chlorobenzene, dichloroethylene/ethanol (20:80), methanol, ethanol/water, allyl alcohol, 2,4-dimethyl-3-pentanol, benzyl alcohol, THF, tetrahydrofurfuryl alcohol, dioxane, glycol ethers, acetone, glycol ether esters, acetic acid, lower aliphatic esters, acetonitrile, nitromethane, DMF, DMSO (chloroform and chlorobenzene for syndiotactic polymers)	(59)
Nonsolvents	Saturated hydrocarbons, mesitylene, carbon tetrachloride (sw), ethanol (anhydrous, sw), ethylene glycol, cyclohexanol, diethyl ether (anhydrous, alcohol free), higher esters ($C > 5$), carbon disulfide, water (sw), dilute acids, dilute alkalies, (benzene and acetone for syndiotactic polymers)	(59)

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Poly(vinyl alcohol)

P. R. SUNDARARAJAN

ACRONYM, TRADE NAMES PVA, Vinol, Airvol® (Air Products and Chemicals), Elvanol® (du Pont), Gelvatol® (Monsanto), Mowiol® (Hoechst), Poval® (Kuraray, Japan), Gohsenol® (Nippon Gohsei, Japan), CCP (Chang Chun, Taiwan).

CLASS Vinyl polymers

STRUCTURE $CH_3CHOH(CH_2{-}CHOH)_n$

MAJOR APPLICATIONS Paper and textile sizing, oxygen resistant films, adhesives, emulcifiers, colloid stabilizers, base/coatings for photographic films, food wrappings, desalination membranes, electroluminescent devices, and cement coatings.

GENERAL INFORMATION Commercial poly(vinyl alcohol) is derived from poly(vinyl acetate). Typical commercial molecular weight ranges for different viscosity grades are: $M_n = 25{,}000$ (low, 5–7 cP), 40,000 (intermediate, 13–16 cP), 60,000 (medium, 28–32 cP) and 100,000 (high, 55–65 cP). (Viscosities correspond to 4% aqueous solution.)[1]

World-wide production >500,000 tons yr^{-1}, two-thirds in Japan, China and Taiwan. Price \$2.65 kg^{-1}(1995).[2]

PROPERTIES OF SPECIAL INTEREST Water soluble; resistant to solvents, oil, and grease; exceptional adhesion to cellulosic and other hydrophilic surfaces.

Synthetic Aspects

STEREOREGULARITY	PARENT POLYMER	SYNTHETIC CONDITIONS	METHOD OF CHARACTERIZATION	CHARACTERISTICS*	REFERENCE
Atactic	PVAc	Free radical, BEt_3/air or AIBN/$h\nu$, −78 to 90°C, amyl acetate or MEK solvent	NMR	—	(3)
Syndiotactic	Poly(vinyl trifluoroacetate)	n-Bu_3B/air, −78°C, heptane	NMR	m: 39%, r: 61%	(4)
		Benzyl peroxide, 60°C	IR, X-ray diffraction	—	(5)
Syndiotactic	Poly(vinyl pivalate)	Radical polymeriation of VP at −40°C; n-hexane	NMR, DSC	r: 69%	(6)
Isotactic	Poly(vinyl t-butyl ether)	BF_3 etherate, −78°C, toluene	NMR	m: 67–76%, r: 33–24%	(4)
		BF_3 etherate, −78°C, toluene	IR, X-ray diffraction	—	(5)
Isotactic	Poly(vinyl benzyl ether)	Cationic polymerization with BF_3 etherate at −78°C			
		In n-heptane/toluene mixture	X-ray diffraction, IR	—	(7)
		In toluene	NMR	m: 93%, r: 7%	(8)
		In nitroethane	NMR	m: 76%, r: 24%	(8)

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STEREOREGULARITY	PARENT POLYMER	SYNTHETIC CONDITIONS	METHOD OF CHARACTERIZATION	CHARACTERISTICS*	REFERENCE
Isotactic	Poly(*t*-butyl vinyl ether)	BF_3 etherate, in toluene, at −78°C	NMR, X-ray	*i*: 79.1, *h*: 18.9, *s*: 2.0; DP: 3,540 *i*: 77.8, *h*: 19.6, *s*: 2.6, DP: 23,800	(9)
Isotactic	None. Direct polymerization of vinyl alcohol monomer	Vinyl alcohol was formed through acid catalyzed hydrolysis of ketene methyl vinyl acetal. Kinetics of tautomerization to acetaldehyde was controlled to extend the half life of vinyl alcohol to enable polymerization. Also copolymerization with maleic anhydride and acrylonitrile.			(10)
Head-to-head	PVAc	Benzyl peroxide, 25–110°C, $M_w = 16.5 \times 10^4 - 4.07 \times 10^4$	1,2 diol content	1.23–1.95 mol %	(11)
		Free radical, BEt_3/air or AIBN/$h\upsilon$, −78 to 90°C	1,2 diol content	1.16–1.98%	(3)

**m*: meso diad; *r*: racemic diad; *i*: isotactic triad; *h*: heterotactic triad; *s*: syndiotactic triad

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat of polymerization	$kJ\,mol^{-1}$	Polymerization of acetaldehyde (at 298.15 K)	64.5	(12)
Density	$g\,cm^{-3}$	% Acetate content		(13)
		0	1.329	
		10	1.316	
		20	1.301	
		30	1.288	
		40	1.274	
		50	1.260	
		60	1.246	
		70	1.232	
Specific gravity	–	Gelvatol	1.19–1.27	(14)
		Airvol	1.27–1.31	(15)
Index of refraction n_D^{20}	–	% Acetate content	1.557	(13)
		0	1.548	
		10	1.539	
		20	1.530	
		30	1.521	
		40	1.512	
		50	1.503	
		60	1.494	
		70		
		Airvol	1.55	(1, 15)
Coefficient of linear expansion		Elvanol	$0.7–1.2 \times 10^4$	(13)
		Gelvatol, plasticized	1×10^{-4}	(14)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Thermal conductivity	$W m^{-1} K^{-1}$	Airvol	0.2	(1, 15)
Specific heat	$J g^{-1} K^{-1}$	Airvol	1.5	(1, 15)
			1.67	(2)
Glass transition temperature T_g	K	–	358	(16)
		Airvol	348–358	(1, 15)
		87–89% hydrolyzed	Empirical formula (°C): $58 - (2.0 \times 10^{-3}/DP)$	(2)
Heat capacity	$J K^{-1} mol^{-1}$	250 K	52.21	(17)
		270 K	57.95	
		290 K	64.50	
		300 K	68.11	
Solubility parameter	$(MPa)^{1/2}$	–	25.78	(18, 19)
Interaction parameter	–	Water, 30°C	0.494	(20)
		Water, 267°C	−0.49	(21)
		Glycerol, 228°C	−0.16	(21)
		Water, 40°C, crystallinity >28%	0.30	(22)
		Water, 40°C, crystallinity 28%	0.18	(22)
Sedimentation coefficient	s	Water, 20°C, $M_w = 13{,}000$	0.96×10^{-13}	(23)
		Water, 20°C	Empirical formula: $s_0 \approx 4.4 \times 10^{-15} \times M^{0.32}$	
Diffusion coefficient	$cm^2 s^{-1}$	Water, 20°C, $M_w = 13{,}000$;	7.46×10^{-7}	(23)
		Water, 20°C, $M_w = 90{,}000$	2.16×10^{-7}	(23)
		o-Positronium	0.5×10^{-6}	(24)
Second virial coefficient	$mol\, cm^3 g^{-2}$	Water, 30°C, $M_w = 18.0 \times 10^4$	3.9×10^{-4}	(23, 25)
		Water, 30°C, $M_w = 19.6 \times 10^4$	5.2×10^{-4}	
		Water, 73.5°C, $M_w = 24.5 \times 10^4$	1.12×10^{-4}	
Theta temperature θ	K	Water	370	(26, 27)
		t-Butanol/water (32/68 w/w)	298	(26, 27)
		Ethanol/water (41.5/58.5 w/w)	298	(27, 28)
		Methanol/water (41.7/58.3 w/w)	298	(27, 28)
		i-Propanol/water (39.4/60.6 w/w)	298	(27, 28)
		n-Propanol/water (35.1/64.9 w/w)	298	(27, 28)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Characteristic ratio ($C_\infty = r_\theta^2/nl^2$)	–	Water, 30°C	8.3	(29)
$d(\ln C)/dT$	deg^{-1}	Thermoelastic method		
		DP 2300, 20–80°C, water or 18% (vol) glycol/water as diluent	0.0	(30)
		Du Pont PA-5 (DP 1600), 20–90°C, water as diluent	-3.6×10^{-3}	(31)
		Elvanol 71/30 (DP 1830), 20–90°C, water as diluent	0.7×10^{-3}	(31)
		Atactic, DP 3100	-1.7×10^{-3}	(32)
		Syndiotactic, DP 3135	-0.6×10^{-3}	(32)
		Isotactic, DP 4470	-2.3×10^{-3}	(32)

Aqueous salt solutions

Salt	Maximum salt concentration in which PVA is soluble (% in water)*		Reference
	98% hydrolyzed	88% hydrolyzed	
Na_2SO_4	5	4	(1)†
$(NH_4)_2SO_4$	6	5	
$NaHCO_3$	9	7	
NaCl:KCl	14	10	
$NaNO_3$	24	20	

*By adding a 10% solution of PVA to 50 ml of the salt solution at incremental concentration until precipitation is observed.
†See reference (1) for other salts. Also see reference (33).

Solvents and nonsolvents

CONDITION	SOLVENT	NONSOLVENT	REFERENCE
–	Glycols (hot), glycerol (hot), piperazine, formamide, dimethyl formamide, DMSO (hot), water	Hydrocarbons, chlorinated hydrocarbons, lower alcohols, tetrahydrafuran, ketones, carboxylic acids, esters, concentrated aq. salt solutions	(34)
Syndiotactic	Water (above 160°C, as a diluent), 1,3-propandiol (above 160°C)	–	(34)
Syndiotactic, $r = 60–64\%$	N-methylmorpholine-N-Oxide/water (70:30), 100°C	–	(35)

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CONDITION	SOLVENT	NONSOLVENT	REFERENCE
12% Acetyl	Water	Hydrocarbons, halogenated hydrocarbons, ketones, carboxylic acids, esters, hot water	(34)
30% Acetyl	Water, alcohols, aqueous solution of various salts	Water above 24°C	(36)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric constant ε'	—	Room temperature, $f = 8.6 \times 10^9$ cps	2.6	(37)
		5% water content (wt), room temperature, $f = 8.6 \times 10^9$ cps	3.0	(37)
		25°C, 0.12×10^6 Hz	5.9	(13)
Loss factor ($\tan \delta$)	—	Room temperature, $f = 8.6 \times 10^9$ cps	40×10^{-3}	(37)
		5% water content (wt), room temperature, $f = 8.6 \times 10^9$ cps	56×10^{-3}	
Tensile strength	MPa	Increases with degree of crystallinity and M_w; decreases with increasing RH		
		Extruded, 25°C	36	(13)
		Partially hydrolyzed, 22°C, 50% RH	42	(1)
		Fully hydrolyzed, 22°C, 50% RH	53	(1)
		98-99% hydrolyzed	67–110	(2)
		87-89% hydrolyzed	24–79	(2)
Elongation at break	%	Extruded, 25°C	225	(13)
		Pressed, 25°C	445	
Young's modulus	GPa	Gel-spun fibers; draw ratio 22 at 200°C; syndiotactic; DP 1150; gel from N-methylmorpholine-N-Oxide/water (70:30)	45	(35)
		Gel drawn (ethylene glycol) films; draw ratio 15 at 0°C; atactic; DP 12,000	37	(38)
Poisson's ratio	—	Gel		(39)
		With DMSO/water	0.455–0.485	
		With ethanol	0.338	
		Hydrogel	0.426–0.447	
Peel strength	$N\ m^{-1}$	On polyester film, Vinol WS-53, partially hydrolyzed, 80% RH	30	(1)
		On polyester film, Vinol WS-53, fully hydrolyzed, 80% RH	12	
Electrical resistivity	ohm cm	Airvol	$(3.1–3.8) \times 10^7$	(1, 15)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Gas permeability coefficient	cm (STP) × cm/ (cm^2 × sec × cmHg)	50% relative humidity, 25°C, atmospheric pressure		(13)
		Oxygen	0.72×10^{-10}	
		CO_2	1.20×10^{-10}	
		Water	$(2{,}900–14{,}900) \times 10^{-10}$	
		Hydrogen	2.14×10^{-10}	
		Acetylene	3.56×10^{-10}	
Surface tension	$mN\,m^{-1}$	1.5% solution concentration, 20°C, $M_w = 88{,}000$, 90% hydrolysis	50	(1, 2)
Interfacial tension	$mN\,m^{-1}$	Gelvatol, $M_w = 96{,}000$; 3% solids, one minute aging; with vinyl acetate	3.3	(14)
Frictional force	volts	Dip coated PVA film on mica		(40)
		Friction force microscopy at 5% RH	0.25	
		Friction force microscopy at 75% RH	1.0–1.25	

Contact angle (θ) and wetting energy ($\gamma \cos\theta$) (erg cm^{-2})* to various polymer films† (33)

Polymer	θ Water	98% Hydrolyzed		88% Hydrolyzed	
		θ	$\gamma \cos\theta$	θ	$\gamma \cos\theta$
PTFE	109.2	104	−15.1	95.0	−4.4
Polypropylene	102.0	95.0	−5.5	89.5	0.5
Polyethylene	96.8	93.2	−2.4	84.8	4.5
Polystyrene	96.1	86.5	3.8	76.0	12.1
Nylon 6	54.6	44.3	44.5	42.4	37.4

*γ for 98% hydrolyzed: 62.4 $mN\,m^{-1}$; γ for 88% hydrolyzed: 49.9 $mN\,m^{-1}$.
†3% aqueous solution, DP 1700.

Resistance to organic solvents* (41)

Solvent	Swelling % (weight)†		Swelling % (area)†	
	98–99% Hydrolyzed	87–89% Hydrolyzed	98-99% Hydrolyzed	87–89% Hydrolyzed
Benzene	−0.6	−1.3	−1.6	−2.4
Iso-octane	−0.5	−1.1	−2.6	−2.3
Carbon tetrachloride	−0.5	−1.1	−2.0	−0.9
Soya bean oil	−0.4	−0.6	−1.2	−1.0

*DP of PVA: 1750.
†Negative signs here denote shrinking, due probably to dehydration.

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Mark–Houwink parameters: *K* and *a*

Solvent	Temperature (K)	$M \times 10^{-4}$	$K \times 10^{3}$ (ml g^{-1})	*a*	Reference
Water	298	2.1	20	0.76	(11)
	298	7	140	0.60	(26, 29)
	303 (syndiotactic rich)	12	73.4	0.63	(42)
	353	46	94	0.56	(25, 29)
Phenol/water (85/15 vol)	303	12	24.6	0.8	(43)
Water	298	—	—	—	(44)
	86.8% hydrolyzed	—	80	0.58	
	93.5% hydrolyzed	25.3	74	0.6	
	96.4% hydrolyzed	24.7	69	0.61	

SPECTROSCOPY	FREQUENCY (cm^{-1})	INTENSITY	ASSIGNMENT	DICHROISM	REFERENCES
Infrared	916	Medium	C–O syndiotactic	⊥	(8, 45, 46)
	1,144	Medium, variable	C–O of doubly hydrogen bonded OH in crystalline domains	⊥	(8, 45, 46)
	1,650	Variable	Adsorbed water	—	(8, 45, 46)
	1,740; 1,265	Variable	Residual acetyl group	—	(8, 45, 46)
	2,910	Strong	CH_2 stretch (Syndio)	⊥	(8, 45, 46)
	2,942	Strong	CH_2 stretch (Atactic)	⊥	(8, 45, 46)
	3,340	Very strong	OH stretching	⊥	(8, 45, 46)
	D916/D849		Tacticity		
		Ratio = 0	90% meso	—	(8, 46, 47)
		Ratio = 1.2	75% racemic	—	(8, 46, 47)
IR of dueterated PVA					(45)
IR of dehydrated PVA					(48)
IR of semicrystalline network					(49)
Positron annihilation					(24)

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SPECTROSCOPY	CONDITION	CHEMICAL SHIFTS (δ, PPM)*	REFERENCES
NMR			(8, 46†, 50, 51) (Reviews)
^{1}H (60, 100 and 220 MHz) spectra	PVA from Kuraray Co., in DMSO-d_6, 20–100°C; tacticity analysis; hexamethyldisiloxane as internal standard	OH proton at 50°C: *i*: 4.52, *h*: 4.33; *s*: 4.10 J(H-O-C-H) (Hz): *i*: 3.1; *h*: 4.3; *s*: 5.3	(52)
^{1}H spectra	Gelvatol 2/75 in DMSO-d_6, at 35°C; tacticity analysis; TMS as standard	OH proton: i: 4.63; *h*: 4.45; *s*: 4.22	(53)
^{13}C (22.63 MHz) and ^{1}H (220 MHz) spectra	Atactic and isotactic PVA ^{13}C in DMSO-d_6, D_2O and hexafluoroisopropyl alcohol; TMS standard ^{1}H in DMSO-d_6; hexamethyldisiloxane standard	^{13}C: CH_2 peaks: DMSO-d_6 / D_2O *rrr*: 45.8 / 47.1 *rrm* + *mrm*: 45.6 / 46.4 *mmr* + *rmr*: 45.2 / 46.1 *mmm*: 44.8 / 45.5 CH peaks: 67.8, 66.2, 64.3 (DMSO-d6); 70.4, 69.0, 67.5 (D_2O)	(54)
^{13}C (22.6 and 67.9 MHz) spectra	Pentad tacticity analysis; atactic and isotactic PVA; in DMSO-d_6 at 80°C; TMS standard	*rmmr*: 68.01; *mrrm*: 64.26 (see reference (55) for others)	(55)
^{13}C (100 MHz) spectra	Heptad and hexad sequence analysis; atactic and isotactic PVA; in DMSO-d_6 and D_2O at 50°C; TMS standard	Atactic: DMSO-d_6 / D_2O Methine *rrrr*: 64.48 / 65.53 *mrrm*: 64.18 / 65.21 Methylene *mrrrm*: 45.92 / 45.07 *rrrrr*: 45.81 / 44.95 (see reference (56) for others)	(56)
^{1}H (360 MHz), 2D NMR	$M_w = 14{,}000$; 70°C; sodium 3-trimethylsilyl [2,2,3,3] propionate as standard	*rr*: 4.062; *mr*: 4.037; *mm*: 3.985; *mmm*: 1.769, 1.675; *rrr*: 1.647	(57)

SPECTROSCOPY	CONDITION	CHEMICAL SHIFTS (δ, PPM)*	REFERENCES
^{1}H (500 MHz) and ^{13}C (125 MHz); 2D NMR	$M_w < 4{,}400$; in D_2O at 80°C; ^{13}C assignments to pentad-hexad level	^{1}H spectra: CH group: 3.957 (*rr*); 3.930 (*mr*); 3.879 (*mm*) CH_2 group: 1.660 (*mmm*); 1.539 (*rrr*) ^{13}C spectra: CH group: 68.18 (*rmmr*); 65.22 (*mrrm*) CH_2 group: 44.85 (*mrrrm*); 44.74 (*rrrrr*) (see reference (58) for others)	(58)
^{1}H (80, 300, and 400 MHz); ^{13}C (100.6 MHz) spectra	$M_w = 50{,}000$; in water at 5–87°C; spin-lattice relaxation times; local chain dynamics; TMS standard	^{13}C spectra at 60°C: CH group: 64.8–65.5 (*rr*); 66.1-66.9 (*mr*); 67.7–68.4 (*mm*) CH_2 group: 43.4–43.9 (*mmm* + *mrm*); 44.7–45.1 (*rrr*)	(59)
^{13}C (50 MHz) VT/MAS solid state spectra	DP 1700, 7600 and 15,500 (Kuraray Co.); phase structure of single crystals from triethylene glycol; TMS standard	CH resonance splits into four peaks at 77.5 (two intra H-bonds); 71.5 (one intra h.bond); 65.0 (no intra H-bond); and 62.4 (intermolecular H-bond); fraction of OH groups with intra H-bond is 0.35 for crystalline domains; decreases from 0.66 (DP 1700) to 0.44 (DP 15,500) in noncrystalline regions	(60)
^{13}C (67.8 MHz) CP/MAS solid state spectra	DP 1700 (Kuraray Co.); study of hydrogen bonding in aqueous gels	–	(61)

*m: meso diad; r: racemic diad; i: isotactic triad; h: heterotactic triad; s: syndiotactic triad.
†References (8, 46, 50, 51) are reviews. Reference (46) presents a chronological review of proton and ^{13}C NMR analysis of PVA and spectral assignments.

Unit cell dimensions

Tacticity	Lattice	Monomers (per unit cell)	Cell dimensions (Å)			Cell angles (degrees)			References
			a	*b**	*c*	α	β	γ	
Atactic	Monoclinic, $P2_1/m$	2	7.81	2.51	5.51	90	97.7	90	(8, 62)
Atactic	Monoclinic, $P2_1/m$ (X-ray and neutron diffraction)	2	7.81	2.52	5.51	90	91.7	90	(63)
Isotactic	–	2	–	2.51	–	–	–	–	(7, 8)

*Chain axis.

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Crystal features

PROPERTY	UNITS	CONDITIONS	VALUE/STRUCTURE	REFERENCE
Crystalline conformation	—	—	Planar zig zag	(45, 62)
Crystal density	$g\,cm^{-3}$	—	1.35	(45, 62)
Melting temperature	K	—	538	(62)*
		69% syndiotactic	531	(6)
		64% syndiotactic, gel drawn fiber, draw ratio 22 at 220°C	540.1	(35)
		Dried gel film, atactic	511.5	(38)
		Dried gel film, syndiotactic	521.5	(38)
Heat of fusion	$kJ\,mol^{-1}$	—	7.11	(6, 62, 64)
		69% syndiotactic	7.5	
Entropy of fusion	$J\,K^{-1}\,mol^{-1}$	518 K	13.1	(13, 64)
Chain folding	—	Single crystals from 0.03–3% solution of triethylene glycol at 353–443 K	Parallelogram-shaped lamellae, 100-Å thick, long side, 1 μm along {101}; short side, 0.25 μm along {100}	(65, 66)
Crystallinity	%	Solution crystallized from 1,3-propanediol, ethylene glycol or triethylene glycol (values depend on solvent and crystallization temperature)	Syndiotactic: 25–35 Atactic: 43–60 Isotactic: 18–24	(4)
		Solution cast films (annealing at 90-210°C)	Syndiotactic: 40–53 Atactic: 30–60 Isotactic: 20–24	(47)
		Cross-linked hydrogel of Elvanol R73-125G (depends on annealing temperature, time, and cross-link density; improved mechanical properties with crystallinity)	20–70	(67)
		Cross-linked hydrogel of Elvanol R73-125G, slow drying at 25°C (rate of crystallization depends on rate of drying, controlled by different drying agents)	Final crystallinity: 45–70	(49, 67)

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PROPERTY	UNITS	CONDITIONS	VALUE/STRUCTURE	REFERENCE
Crystallinity	%	Dry films	Crystallization kinetics. Avrami exponent $n = 0.67$–0.71 for $T_c = 142$–$182°C$; 1.53 for $T_c = 192°C$	(68)
Crystallite size	Å	X-ray diffraction of drawn fibers		(69)
		Draw ratio 4	34	
		Draw ratio 19.8	121	
Long spacing	Å	X-ray diffraction of drawn fibers		(69)
		Draw ratio 4	85	
		Draw ratio 19.8	182	
		Single crystals, SAXS		(60)
		DP 1700	116	
		DP 15,500	125	

*See also references (6, 8, and 64). Reference (8), p. 501–512, reviews the effect of tacticity and parent polymer on the crystallinity, T_m, T_g, and solubility in water.

Isomorphous copolymers

COPOLYMER	COMPOSITION	TYPE OF ISOMORPHISM*	CHAIN CONFORMATION	REFERENCE
Isotactic/atactic PVA	Entire stereo composition	Type 1	Planar zig-zag	(62)
Ethylene/vinyl alcohol	100-0 mol % of ethylene	Isodimorphism	Planar zig-zag	(70, 71)
Ethylene/vinyl alcohol	100-0 mol % of ethylene	Isodimorphism	Discussion of lattice constants, elastic modulii as a function of composition	(71)

*See references (62 and 70) for definition of types of isomorphism.

Random copolymers of ethylene-vinyl alcohol[72]*

PROPERTY	UNITS	CONDITIONS/ETHYLENE MOL %	VALUE
Short branching	mol %	Solution polymerization, 31%	
		CH_3	1.67
		CH_2OAc	0.12
		1,2-Glycol	0.35
		1,4-Glycol	0.96
Short branching	mol %	Suspension polymerization, 32%	
		CH_3	0.61
		CH_2OAc	0.21
		1,2-Glycol	0.27
		1,4-Glycol	4.5

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PROPERTY	UNITS	CONDITIONS/ETHYLENE MOL %	VALUE
Density	$g\,cm^{-3}$	EVAL®, 27%	1.20
		47%	1.12
Melting temperature	K	27%	464
		47%	429
Glass transition temperature	K	27%	345
		47%	321
Diffusion coefficient of water	$cm^2\,s^{-1}$	32%, 20°C	6.63×10^{-9}
		32%, 60°C	99.0×10^{-9}
		44%, 20°C	0.74×10^{-9}
		44%, 60°C	34.9×10^{-9}

*See also the entry on *ethylene-vinyl alcohol* in this handbook.

Block copolymers[73]

BLOCK COPOLYMER	FRACTION OF OTHER MONOMER	PROPERTY/APPLICATION
PVA–PEO–PVA	25–34 wt%	Low surface tension. Segments crystallize independently
PVA–PPO–PVA	12%	–
PVA–polyacrylic acid	20%	Transparent film with gelatin blends (0-100% blend composition range)
PVA–polyacrylamide-polyacrylic acid	100–95/5	Transparent films with starch (up to 40% (wt) of starch)
Propyl to octadecyl alkanes	–	Prepared by end group modification of PVAc in the presence of Mercaptan of the alkanes; modifier for surface tension and wetting property; protective colloid

Compatible polymers in aqueous solutions*[74]

Polymer	Interaction Parameter† α_{23} (ml^{-1})
Carboxy methyl cellulose	0.059
Methyl cellulose	0.128
Hydroxy ethyl cellulose	0.177
Dextrine	0.290
Poly(methyl acrylate) (20% hydrolyzed)	0.006
Poly(ethyl acrylate) (20% hydrolyzed)	0.074

*DP of PVA: 550–1750, concentration of polymers 10–30%; 88% hydrolyzed.
†Smaller value indicates better compatibility.

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Blends*

OTHER POLYMER	CONDITIONS	CHARACTERIZATION METHOD	MORPHOLOGICAL PROPERTIES	REFERENCE
Poly(N-vinyl-2-pyrrolidone)	PVA $M_w = 25{,}000$, 98.5% hydrolyzed; PVPy $M_w = 360{,}000$; films cast from aqueous solutions	^{13}C CP/MAS NMR (100 MHz) and DSC	Miscible over entire composition range; single T_g increasing from 73.1°C (0% PVPy) to 158.9°C (80% PVPy); T_m of PVA depressed from 218.7°C (0% PVPy) to 186.3°C (80% PVPy); chemical shift changes with composition given; intermolecular hydrogen bond between PVA and PVPy	(75, 76)
Polypyrrole	PVA $M_w = 86{,}000$, 100% hydrolyzed; in situ polymerization of Ppy in PVA matrix	FTIR, X-ray, TGA, DSC, SEM	Miscible over entire composition range; no PVA crystallinity with Ppy >20%	(77)
Cellulose	PVA: Mowiol 8-88, blend film cast from N-methyl-2-pyrrolidinone/3 wt% LiCl	X-ray, dielectric and dynamic mechanical measurements	homogeneous with >60 wt% of cellulose, no crystallinity	(78)
		^{13}C NMR	–	(79)
Poly (3-hydroxybutyric acid)	P(3HB) $M_w = 380{,}000$; atactic PVA: DP 2000; syndiotactic PVA: DP 1690; isotactic PVA: DP 7250; films cast from solutions of hexafluoroisopropyl alcohol	FT-IR	Suppression of P(3HB) crystallization is more with syn-PVA than with a-PVA. i-PVA has no influence.	(80)
Starch	Poly(ethylene-vinylalcohol) copolymer, 56% VA; waxy maize, native corn and high-amylose starches; extrusion-blended	X-ray, DSC, SEM, TEM	Phase separated starch domains. Oriented droplets, 0.05–5 μm in length (waxy maize), 0.05–1.2 μm domains (native corn), <0.25 μm (high amylose)	(81)
Nylon 4,6	Poly(ethylene-vinylalcohol) copolymer, 27 mol% ethylene, 13 mol% vinyl acetate; nylon 4/nylon 6: 69/31 mol%; films cast from formic acid	FT-IR, X-ray, DSC, tensile tests	Miscible when nylon 4,6 <35 wt%. C–O···N–H hydrogen bond between nylon and EVOH. Increase in tensile strength from 4 for 15/85 wt% nylon/EVOH to 331 kg cm^{-2} for 100/0 blend	(82)
Copolyamide (random 1:1:1 nylon 6/nylon 6,6/nylon 6,10 units)	M_w of PVA: 24,000; solution cast from N,N-dimethyl formamide	FT-IR, DSC	Miscible in the amorphous state; two phases when quenched after DSC scan; blends exhibit LCST behavior; both components show mutual T_m depression	(83)

*See also gels below for gelation with blends.

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Gels

GELLING AGENT	CONDITIONS	FEATURES	REFERENCES
Ethylene glycol	Syndiotactic ($r = 57\%$) and atactic ($r = 50\%$)	T_m of wet gel: 131°C for a-PVA and 144°C for s-PVA; T_m of dry gel: a-PVA: 231°C (quick cool), 238.5 °C (gradual); s-PVA: 247.5°C (quick cool), 248.5°C (gradual)	(38)
Ethylene glycol/ water	DP of PVA: 1700, 99.9% hydrolyzed	Maximum elastic modulus with 35 mol% of EG	(84)
Water	PVA blended with poly(styrene sulfonic acid) sodium salt	Dried, drawn blend hydrogels; physical cross-links due to interpolymer complex increasing the Young's modulus with NaPSS content; contraction upon absorbing water, with nonideal rubber elasticity	(85)
Water	PVA blended with poly(styrene sulfonic acid) sodium salt; high water content	Three dimensional honey-comb structure, with bundles or tapes (0.1–0.2 μm); highly transparent; permeability similar to that of commercial soft contact lens	(86)
DMSO/water	DMSO/water: 100/0 to 50/50	–	(87)
Water	Telechelic PVA was used to cross-link with chitosan or PVA	Firm network	(88)
Water	Gel prepared by chemical cross-linking with glutaraldehyde, annealing and then hydrated, or low temperature crystallization from aqueous mixtures of glycerol, ethylene glycol, or DMSO	–	(89)
Borax	0.1% solution wt	Thermally irreversible, bisdiol complex formed	(1)*
Boric acid	Full gelation above pH 6	–	(1)
Congo red	3% (w/w) with fully hydrolyzed PVA	Colored gel	(13)
	DP 1800, 99.96% hydrolyzed	Sol-gel transitions	(22, 93-95)

GELLING AGENT	CONDITIONS	FEATURES	REFERENCES
Resorcinol, 2,4-dihydroxybenzoic acid	—	Colorless, thermoreversible gel	(13)
Water, glycerine, glycol	Moviol (Hoechst) $M_n = 48,000$; 2% actetate content	Crystalline gels; crystallinity: PVA (initial): 21.5% Water gel: 21.5% Glycerine gel: 34% Glycol gel: 42%	(96)

*See references (90–92) for DP and concentration effects.

Comonomers and plasticizers

ADDITIVE/OTHER MONOMER	FUNCTION	CONDITIONS	PROPERTY	REFERENCES
Maleic, fumaric or Itaconic acid	Copolymer with PVA	PVA from solution polymerization of vinyl acetate with comonomers	Increased water solubility in the range of 50–100% hydrolysis, controlling flocculation/dispersion of clay, compatibilization with starch	(97)
Catioinic acrylamide or methacrylamide	Copolymer with PVA	—	Adsorption to pulp surface, protective colloid for emulsion polymerization, affinity to acidic dyestuff (e.g., in ink-jet printing)	(97, 98)
Acrylonitrile, vinylidene chloride, ethylenimine, acrylic esters, vinyl chloride, alkali cellulose	Graft copolymer	In solution, free radical, or ionic catalysts	Reduced water sensitivity, film, and coating applications	(13)
Methyl methacrylate	Graft copolymer	PMMA wt% 23–72	Lamellar phase separated morphology; T_g of PMMA *increased* by 20 K; T_m of PVA decreased with increasing PMMA wt fraction	(99)

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ADDITIVE/OTHER MONOMER	FUNCTION	CONDITIONS	PROPERTY	REFERENCES
N-Succinimido (N) thiocarbonyl acrylamide; acrylamide	Graft copolymer	Grafting using a potassium bromate-thiourea redox system	Grafting efficiency up to 45% with STAA; up to 80% with acrylamide	(100)
Styrene	Graft copolymer	Dispersion polymerization of styrene in the presence of PVA-$CuCl_2$ complex	Narrowing of particle size distribution with increased grafting	(101)
		Living polystyrene with vinylsilane end group grafted to PVAc and subsequently saponified	–	(102)
Iodine	Complexing agent	Partially hydrolyzed PVA	Iodine coloring increases with blockiness of acetyl groups (0.05-0.41, arb. units); gold colloid stability increases in parallel	(90)
		Atactic, syndiotactic	Linear polyiodide intercalaction	(103)
		Partially formalized PVA, DP 560	Polyiodide complexation (SAXS); number of iodine atoms per chain increases from 4.2 to 24.9 in the I_2 conc. range 4.0×10^{-4} to 3.1×10^{-3} mol l^{-1}	(104)
Glycerol	Plasticizer	0 wt% in PVA 12% 20% 60%	T_m of PVA = 508 K 497 K 488 K 468 K	(41)
Dipropylene glycol, ethylene glycol	Plasticizers	–	–	(41)
Glyoxal, urea-formaldehydes, trimethylolmelamine	Cross-linking agents	Acid catalysts	–	(1)
Isobutanol, *n*-butanol, phenol, $Ca(SCN)_2$, NaSCN, NH_4SCN	Viscosity stabilizers for aqueous solutions	–	–	(33)

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PROPERTY	CONDITIONS	VALUE	REFERENCE
Flammability	—	Burns similar to paper	(2)
Thermal stability	—	Gradual discoloration above 100°C; darkens rapidly above 150°C; rapid decomposition above 200°C	(2)
Half decomposition temperature	Temperature at which the polymer loses half its weight, if heated in a vacuum for 30 min	268°C	(105)
Initial decomposition temperature	—	240°C	(105)
Thermal decompositon products	240°C, 4 h		(21, 106)
	Water	33.4%	
	CO	0.12	
	CO_2	0.18	
	Acetaldehyde	1.17	
	Acetone	0.38	
	Ethanol	0.29	
	Others	—	
	98% hydrolyzed, 400–500°C		(2)
	Water	73.88%	
	Methanol	0.56%	
	Acetone	0.85%	
	Ethanol	1.25%	
	Acetic acid	6.98%	
	Others	—	
	As a function of hydrolysis	Detailed data	(107)
Biodegradation	—	Degradation products: water, CO_2 Varieties of microorganism (at least 55 known) degrade PVA (e.g., Acinetobacter, E. coli, Pseudomonas (19 species), Saccharomyces, Lipomyces etc.) Degradable in activated sludge, soil landfills, septic systems	(2, 108)

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Dedicated to the memory of my son, Anand.

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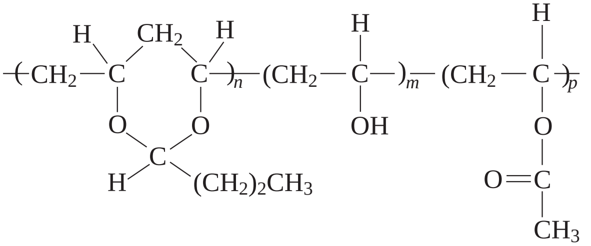
Poly(vinyl butyral)

P. R. SUNDARARAJAN

ACRONYMS, TRADE NAMES PVB, Butvar® (Monsanto), Butacite® (Du Pont), Vinylite XYHL® (Union carbide), Rhovinal® B (Rhone-Poulenc), Movital® (Hoechst), S'Lec® (Shekisui), Saflex® (Monsanto), Trosofoil (Hüls).

CLASS Polyvinyl

STRUCTURE



This schematic should not be construed as a block structure.

MAJOR APPLICATIONS The significant use is in lamination of safety glass (automotive windshields). Others are structural adhesives, binders for rocket propellants, ceramics, in metallized brake linings, lithographic and offset printing plates, magnetic tapes, powder coatings; binder matrix in photoactive, elecrooptic and electronic devices, protective coatings for glass, metal, wood, and ceramics; in wash primers for protecting metal surfaces (e.g., naval vessels); adhesion promoter in inks; dispersions used in textile industry to improve abrasion resistance and reduce color crocking.[1–3]

PROPERTIES OF SPECIAL INTEREST Resistance to penetration by natural wood oils, film clarity, heat sealability, adhesion to a variety of surfaces, chemical and solvent resistance, physical toughness.

GENERAL INFORMATION Poly(vinyl butyral) (PVB) is a member of the class of poly(vinyl acetal) resins. It is derived by condensing poly(vinyl alcohol) (PVA) with butyraldehyde in the presence of a strong acid. PVA reacts with the aldehyde, to form six-membered rings primarily between adjacent, intramolecular hydroxyl groups, leading to the structure shown above.

An example of the compositions of a commercial resin (Butvar) is as follows:[1,4]

Resin type	Molecular weight $(M_w) \times 10^{-3}$	Vinyl alcohol content (wt%)	Vinyl acetate content (wt%)
Butvar B-72	170–250	17–20	0–2.5
Butvar B-76	90–120	11–13	0–1.5

PVB is plasticized for specific applications. Saflex contains 32 phr (parts per hundred resin) of di-*n*-hexyl adipate. Butacite is PVB plasticized with 38.5 phr tetraethylene glycol di-*n*-heptanoate.

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COMMERCIAL PRODUCTION Worldwide unplasticized PVB production was 68,000 tons in 1994. Of this, 66,000 tons were plasticized and extruded for safety glass application. Major interlayer lamination producers are Monsanto (Saflex), Du Pont (Butacite), Shekisui (S'Lec), and Hüls (Trosofoil).[1,5]

Synthetic Aspects

POLYMER	SYNTHETIC CONDITIONS	METHOD OF CHARACTERIZATION	CHARACTERISTICS	REFERENCE
Poly(vinyl butyral)	From PVA, 99% hydrolyzed; condensation of butyraldehyde with PVA in ethanol; H_2SO_4 as catalyst; 53–100 g aldehyde to 100 g PVA; 5–7 h at 75–77°C	—	$M = 70{,}000$; residual PVA decreasing from 25.4–12%, with increasing aldehyde addition	(6)
Poly(vinyl formal)*	From PVA, DP 1000; *i*: 56%, *h*: 32%, *s*: 12%; formalization in 0.1 N HCl aqueous solution at 60°C	^{1}H NMR	Formalization: 84 mol% *Cis*† ring: 70% *Trans*† ring: 14% Rate constant: 8.8×10^{-2} L mol^{-1} h^{-1}	(7)
	From PVA, DP 1000; *i*: 23%, *h*: 47%, *s*: 30%; formalization in 0.1 N HCl aqueous solution at 60°C	^{1}H NMR	Formalization: 87 mol% *Cis*† ring: 59% *Trans*† ring: 28% Rate constant: 6.6×10^{-2} L mol^{-1} h^{-1}	
	From PVA, DP 1000; *i*: 17%, *h*: 46%, *s*: 37%; formalization in 0.1 N HCl aqueous solution at 60°C	^{1}H NMR	Formalization: 87 mol% *Cis*† ring: 50% *Trans*† ring: 37% Rate constant: 6.2×10^{-2} L mol^{-1} h^{-1}	
Poly(vinyl butyral)	Reaction at 10 and 70°C; up to 1,000 h		At 10°C, *cis/trans* ratio is ~5, no significant change with time; at 70°C, ratio decreases from ~5 to ~3 up to 1 h, then increases with time to ~7 after 100 h	(8)
Poly(vinyl butyral)	PVA DP: 1600; 97.5–99.5% hydrolyzed; reaction at 10–60°C, in water, H_2SO_4 or HCl as catalyst (method I); catalyst and aldehyde added to PVA suspension in MEK (method II); aldehyde added in one step or in stages	NMR	Degree of acetalization: 75% (10°C, 3.5 h, method I) 45% (temperature ramp from 18–60°C, 2 h, method I) 85% (30°C, 2 h, method II)	(9)

POLYMER	SYNTHETIC CONDITIONS	METHOD OF CHARACTERIZATION	CHARACTERISTICS	REFERENCE
PVB-*g*-PDMS	PVB as above, with 45% acetalization	NMR	M_w: 690×10^3; degree of grafting: 42%	(9)
PVB-*g*- PEO	PVB as above, with 45% acetalization	NMR	M_w: 920×10^3; degree of grafting: 35%	(9)
PVB-linear hemiacetal	Acid treatment (1 N HCl) of PVB in methanol solution (4% w/v)	NMR	Acid hydrolysis of *trans* rings leads to stable, linear hemiacetal; *cis* rings are not affected; slow conversion to PVB at room temperature over 12 months	(10)
Ionomeric PVB: poly(vinyl butyral-*co*-vinyl benzal sodium (or potassium) sulfonate)	PVA DP 550, 1275, and 1800; Na-salt of *o*-benzaldehyde sulfonic acid (BSNA) reacted with PVA. Nitric acid catalyst, 19-22°C; followed by reaction with butyraldehyde. BSNA-PVA reaction hindered above 60°C	NMR, DSC, viscosity, rheology	1–15 mol% ionomer groups; T_g increases with ionomer content from 73–106°C (0–15%); 18–20% residual PVA	(11)

*This polymer is included here to illustrate the effect of parent PVA tacticity on the ring conformation of the acetal.
†The *cis* is also referred to as the ''meso'' ring, and *trans* as the ''racemic'' ring in the literature.

General Properties

PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Specific gravity	–	Butvar		(1, 2, 4)
		B-72	1.1	
		B-76	1.083	
		Butacite	1.07	(12)
Refractive index	n_D^{23}	Butvar		(1, 2, 4)
		B-72	1.49	
		B-76	1.485	
		Butacite	1.47–1.50	(12)
Density	$g\,cm^{-3}$	–	1.091	(14)
		28% triethylene glycol-di-(2-ethylbutyrate) plasticizer	1.078	
Tensile yield strength	MPa	Butvar	47–54	(1, 2)
		B-72	40–47	
		B-76		

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PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Tensile strength	MPa	Films from Butvar BR aqueous dispersion		(3)
		No plasticizer	41–48	
		40–50 phr plasticizer	14	
		18% hydroxyl content; $M_w \approx 70{,}000$; plasticized with dibutyl phthalate		(6)†
		0 phr DBP	56	
		15 phr DBP	36	
		37.2 phr DBP	38	
Elastic modulus	$MPa \times 10^3$	Butvar		(1, 2)
		B-72	2.28–2.34	
		B-76	1.93–2.0	
Storage modulus	MPa	PVB with 32 phr di-*n*-hexyladipate (Monsanto Saflex); 1 Hz	3.98×10^2	(15)
		Above, neat resin	1.86×10^3	
Elongation at break	%	Butvar		(1)
		B-72	70	
		B-76	110	
		Butacite	>200	(12)
Elongation at yield	%	Butvar		(1)
		B-72	8	
		B-76	8	
		18% hydroxyl content; $M_w \approx 70{,}000$; plasticized with dibutyl phthalate		(6)†
		0 phr DBP	9	
		15 phr DBP	10	
		37.2 phr DBP	380	
Flexural strength	MPa	Butvar		(1, 2)
		B-72	83–90	
		B-76	72–79	
Impact strength	$J\,m^{-1}$	Izod, notched, 1.25×1.25 cm, Butvar		(1, 2)
		B-72	58.7	
		B-76	42.7	
Glass transition temperature	K	Butvar		(1, 2)
		B-72	345–351	
		B-76	335–345	
		Triethylene glycol-di-(2-ethylbutyrate) plasticizer		(14)
		0%	332.3	
		28%	272	

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PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Glass transition temperature	K	Butvar with di-*n*-hexyl adipate		(16)
		0%	353	
		10 phr	333	
		32 phr (from mechanical loss spectroscopy at 1 Hz)	302	
		18–20% (wt) hydroxyl content	346	(11)
		As above, 5% ionomer	358	
		As above, 15% ionomer	379	
Softening temperature	K	With 25% residual PVA	338	(6)†
		As above, with 30 phr dibutyl phthalate	303	
		With 12.1% residual PVA	321	
		As above, with 30 phr dibutyl phthalate	291	
Specific heat	$J (g K)^{-1}$	Triethylene glycol-di-(2-ethylbutyrate) plasticizer		(14)
		0%	1.36	
		28%	1.90	
Thermal conductivity	$W (m K)^{-1}$	Butvar with di-*n*-hexyl adipate		(16)
		0%	0.236	
		10 phr	0.275	
		32 phr	0.272	
Heat sealing temperature	K	Butvar		(1)
		B-72	493	
		B-76	473	
Dielectric constant	–	Butvar		(2)
		B-72 50 Hz	3.2	
		B-72 10 MHz	2.7	
		B-76 50 Hz	2.7	
		B-76 10 MHz	2.5	
Dissipation factor	–	Butvar		(2)
		B-72 50 Hz	6.4×10^{-3}	
		B-72 10 MHz	31×10^{-3}	
		B-76 50 Hz	5.0×10^{-3}	
		B-76 10 MHz	15×10^{-3}	
Relaxation temperatures	K	DMA and DSC analysis; PVB with 32 phr di-*n*-hexyladipate (Monsanto Saflex)	226 (β); 285 (α_2); 304 (α_1)	(17)
Surface tension	$mN m^{-1}$	–	38	(18)
Critical surface tension	$mN m^{-1}$	PVB with 12 or 30% hydroxyl content, with polyhydric alcohols	24–25	(5, 19)

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PROPERTY	UNITS	CONDITIONS*	VALUE	REFERENCE
Partial specific volume	$cm^3\ g^{-1}$	Amyl alcohol, 20°C; $[\eta] = 122\ cm^3\ g^{-1}$	0.883	(20)
Second virial coefficient	$mol\ cm^3\ g^{-2}$	Dioxane, 37°C; M_w =		(20)
		$57.5–181 \times 10^3$	$9.45–12.2 \times 10^{-4}$	
		$73.9–208 \times 10^3$	$9.15–11.3 \times 10^{-4}$	
		$89.5–541 \times 10^3$	$5.53–10.3 \times 10^{-4}$	
		M_w = 68,500, 25°C		(21, 22)
		Acetic acid	10.4×10^{-4}	
		3:1 MIBK/MeOH	7.9×10^{-4}	
		1:1 MIBK/MeOH	3.6×10^{-4}	
		9:1 MIBK/MeOH	1.6×10^{-4}	
Solubility parameter	—	Theoretical estimate of dispersion (δ_d), polar (δ_p) and hydrogen bonding (δ_h) contributions to solubility parameter:		(23)
		δ_d	7.72	
		δ_p	2.90	
		δ_h	3.26	
		δ_{total}	8.87	
		Low hydrogen bonding solvents:		(1)
		Hydroxyl content 9–13%	9.0–9.8	
		Hydroxyl content 17–21%	Insoluble	
		Medium hydrogen bonding solvents:		(1)
		Hydroxyl content 9–13%	8.4–12.9	
		Hydroxyl content 17–21%	9.9–12.9	
		High hydrogen bonding solvents:		(1)
		Hydroxyl content 9–13%	9.7–12.9	
		Hydroxyl content 17–21%	9.7–14.3	

*phr = parts per hundred resin.
†Reference (6) discusses the effect of plasticizers on various acetals.

Solvents and Nonsolvents

CONDITIONS	SOLVENTS	NONSOLVENTS	PARTIALLY SOLUBLE IN	REFERENCE
Butvar B-72	Acetic acid (glacial), butanol, cyclohexane, dioxane, ethyl Cellosolve, ethylene chloride, methanol, toluene/ethanol (60:40 wt), xylene/butanol (60:40 wt)	Acetone, butyl acetate, carbon tetrachloride, diisobutyl ketone, hexane, methyl ethyl ketone, methyl isobutyl ketone, nitropropane, toluene, xylene	Diacetone alcohol, isophorone, methylene chloride	(1, 3)

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CONDITIONS	SOLVENTS	NONSOLVENTS	PARTIALLY SOLUBLE IN	REFERENCE
Butvar B-76	Acetic acid (glacial), acetone, butanol, butyl acetate, cyclohexane, dioxane, ethyl Cellosolve, ethylene chloride, methyl acetate, methyl ethyl ketone, methyl isobutyl ketone, toluene	Carbon tetrachloride, hexane, methanol, nitropropane, xylene	—	(1, 3)
PVB, 20% hydroxyl content	Acetic acid	Methanol	—	(21, 22)*
70% acetylation	Alcohols, cyclohexane, ethyl lactate, ethyl glycol acetate	Hydrocarbons, methylene chloride, aliphatic ketones	—	(24)
83% acetylation	Methylene chloride, alcohols, ketones, lower esters	Hydrocarbons, methanol, higher esters	—	(24)

*The effect of temperature and solvent on solubility and aggregation is discussed in references (17) and (18).

Mark-Houwink parameters: K and a[25]

Solvent	Temp. (°C)	$M \times 10^{-4}$	$K \times 10^4$ (ml g^{-1})	a
Tetrahydrafuran	25	5.8–17 (20% hydroxyl content)	2.89	0.72
Tetrahydrafuran	25	12 (10% hydroxyl content)	2.52	0.72

Spectroscopy

SPECTROSCOPY	FREQUENCY (cm^{-1})	INTENSITY	ASSIGNMENT	OBSERVATIONS	REFERENCE
Infrared	1,383, 1,136, 1,111, 1,052, 1,000, 971	—	1,136 and 1,000 cm^{-1} bands to cyclic acetal	—	(5)
	3,448	Weak	Vinyl alcohol	—	(5)
	—	—	—	—	(26)

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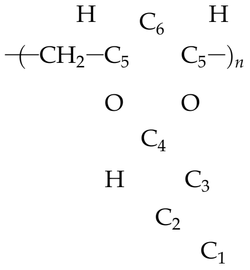
SPECTROSCOPY	CONDITIONS	CHEMICAL SHIFTS (D, PPM)/ OBSERVATIONS	REFERENCE
Numbering scheme		This numbering scheme is used here to refer to the chemical shifts	
^{1}H (100 MHz) spectra	Study of the effect of PVA tacticity on the *cis* and *trans* configuration in poly(vinyl formal): close cousin of PVB; DMSO as solvent; TMS standard	$O{-}CH_2{-}O$ resonance as a quartet at 4.55 and 4.85 ppm for *cis* ring; singlet at 4.7 ppm for *trans* ring; *i*-PVA leads to high *cis* formal	(7, 27)
^{13}C (75 MHz) and ^{1}H (300 MHz) 2-D NMR spectra	DMSO-d_6 as solvent/standard, at 100°C, interpretation and spectral assignments	^{13}C spectra: C_2: 16 C_3: 36 ppm; C_4: 100.2 (*cis* ring), 93.5 (*trans* ring) ^{1}H spectra: $H(C_4)$ 4.51, 4.49, 4.47 (*cis*); 4.79, 4.77, 4.75 (*trans*)*	(28)
^{13}C (100 MHz) and ^{1}H (400 MHz) spectra	$M_w = 200{,}000$; 18.5% (wt) residual PVA; *d*-benzene or methanol as solvent, 25°C	^{13}C spectra: C_4: 102.7 ppm (*cis* ring); 95.9 (*trans*) Acetal ring conformations are related to the rotational isomeric states of meso and racemic diads of parent PVA	(29)
^{13}C (22.6 and 62.9 MHz) spectra	PVB with 35% (mol) acetalation, in acetone-d_6; hexamethyldisiloxane standard	C_1, C_2, C_3, C_4 at 14, 18, 36, and 102 ppm, respectively; microdynamics of side chain motion discussed	(30)
^{13}C CP/MAS (15 MHz) spectra	Butvar and with 32 phr di-*n*-hexyladipate (Monsanto Saflex)	C_4 at 103 ppm; $T_1\rho$ (C) decreases from 21 ms to 7 ms with 0–32 phr plasticizer. Two phase character: soft regions of the sample are associated with liquid plasticizer containing mobile polymer; hard regions contain solid polymer with immobilized plasticizer	(16)

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SPECTROSCOPY	CONDITIONS	CHEMICAL SHIFTS (D, PPM)/ OBSERVATIONS	REFERENCE
^{13}C (100 MHz) CP/MAS NMR	PVB with 32 phr di-*n*-hexyladipate (Monsanto Saflex); 25–115°C	C_1, C_2, C_3, C_4 at 15, 18, 38, and 102 ppm, respectively; peak width variations with temperature are related to glass transition and chain mobility	(17)
^{13}C (100.6 MHz) CP/MAS spectra	PVB with 32 phr di-*n*-hexyladipate (Monsanto Saflex), and neat resin; 23°C	C_4 at 102 ppm; $T_1\rho$ (H) decreases from 3.5 ms (neat resin) to 1.4 ms with 32 phr DHA; microheterogeneous phase structures discussed. Estimated rigid fraction is 0.61 for neat PVB, 0.45 for PVB/DHA	(15, 31)
^{13}C (75 MHz) CP/MAS spectra	$M_w = 100{,}000$; 14% PVA; composite films with tributyl citrate and alumina; 20% (wt) TBC; films from 55/45 (wt) toluene/ethanol; Alocoa alumina, 5 μm particles, 88% (wt) alumina, 12% polymer	C_4 at 102 ppm; $T_1\rho$ (H): 2.3 (neat), 4.6 (with alumina), 1.3 (with TBC), 2.6 ms (with alumina/ TBC) C_1 at 15 ppm; $T_1\rho$(H): 4.2 (neat), 5.5 (with alumina), 0.96 (with TBC), 2.4 ms (with alumina/ TBC)*	(32)

*See reference for others.

Optical and electrical properties (film dip-coated from cyclohexane solution)[33]

CONDITION	UV-VIS ABSORPTION MAXIMUM (nm)	ABSORPTION	OPTICAL BAND GAP ENERGY (eV)	ACTIVATION ENERGY (eV)	CONDUCTIVITY AT 315 K, $\times 10^{-12}$ ($S\,m^{-1}$)
PVB	338	0.590	3.27	0.83	0.114
PVB + 5% I_2	366	0.425	2.57	0.79	2.239
PVB + 10% I_2	–	–	2.40	0.74	6.310
PVB + 15% I_2	–	–	2.00	0.65	9.016

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Plasticizers/Fillers

PLASTICIZER/FILLER	CONDITION	OBSERVATIONS	REFERENCE
Dibutyl phthalate, butyl benzyl phthalate, phosphates, dihexyl adipate	—	—	(2)
Dibutyl phthalate	—	T_g reduced by 1.3°C phr of plasticizer	(1)
Di-*n*-hexyladipate	Butvar with various concentrations of plasticizer	Solid state ^{13}C NMR studies, DMA and SANS	(16)
Di-*n*-hexyladipate	—	Solid state ^{13}C NMR studies	(15, 17)
Di-*n*-hexyl adipate	Butvar	Known compatibility limit: 3:1	(4)
Dioctyl adipate	Butvar	Known compatibility limit: 4:1	(4)
Phosphates	Butvar	Known compatibility limit: 1:1	(4)
Phenolics, ureas, melamines, epoxies	—	Cross-linking with PVB, either as a host or guest	(2, 3)
Alumina	—	Solid state ^{13}C NMR study of chain mobility	(32)
Tributyl citrate	—	Solid state ^{13}C NMR study of chain mobility	(32)
Tri-propyleneglycol dibenzoate	M_w of PVB: 200,000; 18.2% hydroxyl content	2.5% (wt) solution of polymer in plasticizer. Precipitation temperature $T_p = 60$°C (used to determine critical miscibility parameter for polymer/plasticizer)	(34)
Di-propyleneglycol dibenzoate	As above	As above, $T_p = 47$°C	(34)
Di-tetrahydro furural adipate	As above	As above, $T_p = 68$°C	(34)
Di-isoheptyl phthalate	As above	As above, $T_p = 98$°C	(34)

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Blends

OTHER POLYMER	CONDITIONS	TECHNIQUES USED	FEATURES	REFERENCE
Poly(ε-caprolactone) and carbon black	M_w (PVB): 100,000; M_w (PCL): 35,000; Vulcan XC-72 conductive carbon black (5 vol%); CB roll-mixed; blend films from THF solutions; crystallization temperature of 41°C	Optical and atomic force microscopy	Growth rate of PCL spherulites decreased with increasing PVB content; large spherulites (10 mm); CB had no influence on nucleation or growth rate	(35)
	As above and also with fullerene (5 vol%)	Optical microscopy, DSC, electrical resistivity	Spherulites with twisted lamellae; resistivity increased with PVB content; I_{PTC} values*: 0% PVB: 12; 1% PVB: 324; 5% PVB: 673.1	(36)
Poly (ε-caprolactone)	M_w of PCL: 33,000; M_w of PVB: 116,000	Optical microscopy, X-ray diffraction, SAXS	Nucleation density reduced by addition of PVB; large banded spherulites	(37)
Poly(ethylene sebacate)	M_w of PESEB: 19,000; M_w of PVB: 116,000	Optical microscopy, X-ray diffraction, SAXS	–	(37)
Poly(N-vinyl-2-pyrrolidone)	PVB: Mowital B6OHH), 16% hydroxyl content. solution cast films from chloroform	DSC	Single phase with PVP <50 wt% T_g (K) for PVB/PVP ratio (wt%): 0/100 : 436; 50/50 : 377; 70/30 : 362.5; 100/0 : 341	(38)
Polypropylene/mica	Ethylene-propylene block copolymer; PVB and plasticized PVB; 30% (wt) mica	DMA, impact strength, SEM	Addition of up to 14% (wt) of PVB had no effect on tensile strength or modulus. Impact strength decreased with increasing PVB content	(39)

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OTHER POLYMER	CONDITIONS	TECHNIQUES USED	FEATURES	REFERENCE
Polyurethane	M_w of PVB: 170,000; 18.5% hydroxyl content. PU: Tecoflex EG-85A (from methylene bis cyclohexyl diurethane and polytetramethylene ether glycol). Extrusion blended	DMA, DSC, TEM	Miscible over entire composition range, due to interaction of PVB with hard segment. Single T_g, decreasing with PU content. Model compounds of the hard segment are also miscible	(23)
Polyaniline	Solution or melt processing	—	Self-assembled network morphology, onset of electrical conductivity with 1% (vol) of PANI	(40)
Ionomeric PVB: poly(vinyl butyral-*co*-vinyl benzal sodium (or potassium) sulfonate)	Blends up to 50% IPVB; 3% or 5% ion content	NMR, DMA	Storage modulus G' ($N\,m^{-2}$) at 25°C increases from 4.2×10^7 to 8.6×10^7 (0–50% IPVB) with 3% ion content	(41)
Polyacetylene	Synthesized in dilute solutions of PVB	—	40–50% *trans* form of polyacetylene; low defect content	(42)

*I_{PTC}: Intensity of positive temperature coefficient, defined as the resistivity ratio ρ_{max}/ρ_{min}; ρ_{max} is the maximum in the temperature-resistivity curve and ρ_{min} is the resistivity at room temperature.

Resins Compatibility with PVB

PVB TYPE	COMPATIBLE	PARTIALLY COMPATIBLE	INCOMPATIBLE	REFERENCE
Butvar B-2	Nitrocellulose, epoxy (Epi-Rez 540-C, Araldite 6069), isocyanate, phenolic, shellac	Alkyd, cellulose acetate butyrate, ethyl cellulose, rosin derivatives, silicone, urea formaldehyde	Acrylate, cellulose acetate, chlorinated rubber	(4)*
Butvar B-76	Nitrocellulose, epoxy, phenolic, shellac, silicone	Alkyd, cellulose acetate butyrate, urea formaldehyde, vinyl chloride copolymer	Acrylate, cellulose acetate, chlorinated rubber	(4)*

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PVB TYPE	COMPATIBLE	PARTIALLY COMPATIBLE	INCOMPATIBLE	REFERENCE
Shekisui BM-2	Poly (vinylpyrrolidone), poly (vinyl acetate-*co*-N-vinylpyrrolidone), poly (styrene-*co*-maleic acid), poly (styrene-*co*-maleic acid ester) (conditional)	–	Poly(vinylidene chloride), chlorosulfonated polyethylene, polyester, poly(ethylene-*co*-vinyl acetate), poly(butadiene-*co*-styrene), poly-(butadiene-*co*-acrylonitrile), poly(vinyl chloride-*co*-vinyl acetate), poly(vinyl chloride-*co*-vinyl propionate)	(43)

*Consult reference (4) for the trade names of the resins applicable to the entries in this table.

PVB as binder polymer in optoelectronic/photoactive devices

DEVICE	GUEST MOLECULE	APPLICATION	REFERENCE
Xerographic photoreceptor	Squaraine	Dispersion of squaraine in the charge generating layer	(44)
Electrode/ electrolyte tape	Nickel powder	Molten carbonate fuel cells	(45)
Ceramics	Al_2O_3 powder	Ceramic processing aid	(46)
Holograms	Cresyl violet	Hologram recording by spectral hole burning	(47)
Holograms	Chlorin (2,3-dihydroporphyrin)	Holographic recording/storage media	(48)
Optical memory	Anthraquinone derivatives	Spectral hole burning	(49)
Optical memory	Perylene	Spectral hole burning	(50)
Optical memory	Chlorin (2,3-dihydroporphyrin)	Holographic recording	(51)
Optical memory	Chlorophyll A	–	(52)
Optical memory	Porphyrin and phthalocyanine derivatives	Spectral hole burning	(53)
Optical memory	–	Holographic recording	(54)
Electrochromic device	LiCl in PVB gel	–	(55)
Fuel cell	–	Interconnect plate for a planar solid oxide fuel cell	(56)
Photochromism	Spirooxazines	–	(57)

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Thermal Degradation

TEMP. (K)	METHOD	MACHANISM	PRODUCTS/PERCENTAGE		REFERENCE
553–583	TGA, FTIR	Oxidation of copolymer	7%		(58)
583–673	—	PVB thermal oxidation	Butanal, C_4 hydrocarbons, CO_2 and water (71%)		(58)
673–733	—	Oxidation of cyclic and cross-linked compounds	9%		(58)
733–823	—	Oxidation of residual carbon	13%		(58)
773	Pyr-GC/mass spectrometry	—	CO, CO_2	10.2%	(59)*
			Acetaldehyde	4.5	
			Acetone	1.0	
			Butanal	60.8	
			H_2O	1.1	
			Benzene	1.2	
			Alkyl aromatics	0.1	
			Butenal	9.3	
			Acetic acid	2.9	

*See reference (59) for the effects of silica, mullite, α-alumina and γ-alumina on the thermal degradation of PVB.

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Dedicated to the memory of my son, Anand.

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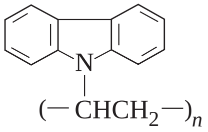
Poly(N-vinyl carbazole)

JOHN H. KO

TRADE NAMES PVK (Polysciences, Inc.), Luvican® (BASF Corp.)

CLASS Vinyl polymers; homopolymers

STRUCTURE



MAJOR APPLICATION Photoconductor

PROPERTIES OF SPECIAL INTEREST High heat distortion temperature and outstanding dielectric properties for electrical uses. High refractive index for optical uses.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile modulus	MPa	–	$(2.5–4.2) \times 10^3$	(1–7)
Tensile strength	MPa	–	14	(1–7)
		Oriented	140	
Flexural strength	MPa	–	35–55	(1–7)
Compressive strength	MPa	–	30–35	(1–7)
Shear strength	MPa	–	20–30	(1–7)
Modulus of elasticity	MPa	Tensile test	3,700	(1–7)
Impact strength	$J\,m^{-1}$	DIN 53453	$(5–10) \times 10^5$	(1–7)
Vicat softening temperature	K	–	~468	(1–7)
Elongation	%	Amorphous	$\ll 1$	(1–7)
		Oriented	1	
Hardness	MPa	Ball indentation	100	(1–7)
Index of refraction n_D	–	At 20°C	1.69	(1–7)
Density	$g\,cm^{-3}$	Amorphous	1.184	(1–7)
		Oriented	1.191	
Glass transition temperature	K	Amorphous	500	(1–7)
		Syndiotactic	549	
		Isotactic	399	

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Poly(N-vinyl carbazole)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Heat capacity (of repeat units)	$kJ\,K^{-1}\,mol^{-1}$	–	3.47×10^{-2}	(1–7)
Linear coefficient of thermal expansion	K	293–373 K	5×10^{-5}	(1–7)
Thermal conductivity	$W\,cm^{-1}\,K^{-1}$	20°C 170°C	1.26×10^{-3} 1.68×10^{-3}	(1–7)
Specific heat	$J\,g^{-1}\,°C^{-1}$	–	1.26	(1–7)
Water absorption	%	–	<0.1	(1–7)
WLF parameters: C_1 and C_2	–	Reference temp. = 220°C	$C_1 = 11.4$ $C_2 = 226.0$	(6)
Solvents	Aromatic hydrocarbons, chlorofom, chlorobenzene, methylene chloride, and tetrahydrofuran			(8, 9)
Nonsolvents	Alcohols, esters, ketones, carbon tetrachloride, and aliphatic hydrocarbons			(8, 9)
Dielectric strength	$mV\,cm^{-1}$	25–150°C	1.1–0.86	(1–5)
Resistivity	ohm cm	DIN 57303 25–150°C	10^{16}–10^{17} $(0.05–8) \times 10^{15}$	(1–5)
Loss factor	–	10^3–3×10^8 Hz 10^4 Hz 10^3 Hz, 200°C	$<10^{-3}$ $(2–6) \times 10^{-4}$ 50×10^{-4}	(1–5)
Permittivity	–	20°C, 50 Hz 1 MHz	3	(1–5)
Dielectric constant	–	104 Hz	3	(1–5)
Breakdown field strength	$kV\,mm^{-1}$	–	50	(1–5)
Optical coefficient	–	Birefrigence/unit strain at 210–235°C	-5.5×10^{-2}	(6)
Suppliers	Polysciences, Inc., 400 Valley Road, Warrington, PA 18976, USA (PVK) BASF Corp., 36 Riverside Avenue, Rensselaer, NY 12144, USA (Luvican®)			

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Poly(vinyl chloride)

ANTHONY L. ANDRADY

ACRONYM, TRADE NAMES PVC, Geon (Goodrich), Vinoflex (BASF), Vestolite (Hüls), Airco (Air Products), SCC (Stauffer)

CLASS Vinyl polymers

STRUCTURE $[-CH_2CHCl-]$

MAJOR APPLICATIONS Poly(vinyl chloride) is used in building applications as rigid formulations in water and sewage pipes, siding, gutters, and downspouts, conduits, and cable coverings. Pipe and conduit application are by far the major use of PVC. It is also used as a plasticized material in membrane roofing, and flooring applications. PVC films are used in packaging of consumer goods.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Suspension polymerization	Diacetyl peroxide, peroxydicarbonates, alkyl peroxyesters and AIBN used as initiator; Cellulose derivatives used as protective colloid			(1)
Bulk polymerization	Two-stage reaction process			(2)
Emulsion polymerization				(1)
Typical comonomers	Vinyl acetate (VAM), ~10–15%			–
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	62.5	–
Typical molecular weight range of polymer M_n	$g\,mol^{-1}$	Polymerization temperature (°C)		(1)
		50	67×10^{-3}	
		57	54×10^{-3}	
		64	44×10^{-3}	
		71	33×10^{-3}	
Polydispersity index (M_w/M_n)	–	Determined by GPC for ordinary suspension-polymerized PVC; Temp. (°C) / $M_n \times 10^{-3}$		(3)
		43 / 58	2.44	
		55 / 44	2.08	
		75 / 26	2.01	
Tacticity	Fraction, *f*, of syndiotactic dyads	Polymerization temperature (°C)		(4)
		55	0.55	
		25	0.57	
		0	0.60	
		−30	0.64	
		−50	0.66	
		−76	0.68	

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PROPERTY	UNITS	CONDITIONS	VALUES				REFERENCE
Degree of branching	%	Polymerization temperature (°C)	$-CH(CH_2Cl)-$	$-CCl(CH_2CH_2Cl)-$	$-CCl(CH_2CHCl(CH_2)_2Cl)-$	$-C-C(H/Cl)(C)-C$	(5)
		45	3.9	<0.1	0.5	<0.1	
		55	4.2	0.2	0.6	0.2	
		65	4.6	0.2	0.8	0.3	
		80	4.9	0.3	1.3	0.3	

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Head-to-head and other irregular structures	Per 1,000 repeat units (VC)	Head to head groups	0.2	(6)
		In-chain double bonds	0.1–0.2	
		Chloromethyl branches	4	
		2-Chloroethyl branches	0.5	
		2,4, Dichlorobutyl branches	1	
		Tertiery chlorine	0.5–1.5	
		Long branches	1	
	Per molecule	Total unsaturation	1	
IR (characteristic absorption frequencies)	cm^{-1} band	Planar syndiotactic sequences	603, 638	(7)
		C–Cl units in isotactic sequences	690	(7)
		Discussion of C–Cl region and curve fitting	–	(8)
UV (characteristic absorption frequencies)	Ultraviolet visible absorption bands for polyene sequences with absorption at 306 nm for $n = 4$ sequences. Assignment of peaks.			(9)
^{13}C NMR	–	PVC solution in trichlorobenzene, 380 K	–	(10)
		PVC solution in *o*-dichlorobenzene, 373 K	–	(11)
		Copolymers with vinyidene chloride	–	(12)
Thermal expansion coefficient	K^{-1}	100°C	4.7×10^{-4}	(1)
		120°C	5.5×10^{-4}	
		140°C	6.2×10^{-4}	
Compressibility	bar^{-1}	100°C	5.2×10^{-5}	(1)
		140°C	6.4×10^{-5}	
Density	$g\,cm^{-3}$	100°C	1.352	(13)
		120°C	1.338	
		140°C	1.332	

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Solvents	Methyl ethyl ketone, cyclohexanone, DMF, toluene, nitrobenzene DMSO, acetone/carbon disulfide				(14–16)
Nonsolvents	Alcohols, hydrocarbons, acetone, nonoxidizing acids				(14–16)
Mark–Houwink parameters: K and a	$K = \text{ml g}^{-1}$ a = None		$(K \times 10^3)^\dagger$	a	
		Cyclohexanone, 20°C	13.7	1.0	(17)
		Tetrahydrofurane, 20°C	3.63	0.92	(18)
		Cyclohexanone, 20–60°C	$18.74 - (4.85 \times 10^{-4})T$	0.803	(19)
		Cyclopentanone, 20–60°C	$0.091 - (1.55 \times 10^{-4})T$	0.861	(19)
		Tetrahydrofurane, 20–50°C	$10.87 - (1.67 \times 10^{-4})T$	0.851	(19)
		$M_n = (0.3–1.9) \times 10^5$	K	a	
		Chlorobenzene, 30°C	0.0712	0.59	(20)
		Cyclohexane, 25°C	0.0138	0.78	(21)
		Tetrahydrofuran, 25°C	0.0163	0.78	(22)
Second virial coefficient	$\text{mol cm}^3\text{ g}^{-2}$	Cyclohexanone, 25°C, M_n = 118,000	11×10^{-4}		(23)
Interaction parameter χ	–	Toluene, 125-140°C	0.45–0.41		(24)
		2-Propanol, 125–140°C	1.10–0.97		(24)
		Methanol, 125–140°C	1.42–1.24		(24)
		Acetone, 125–140°C	0.77–0.53		(24)
		Benzene, 120°C	0.75		(25)
		Carbon tetrachloride	1.14		(25)
		Chloroform	0.91		(25)
		Dichloromethane	1.63		(25)
Theta temperature Θ	K	Cyclohexanone	324		(26)
		Dimethylformamide	309.5		(27)
		Benzyl alcohol	428.4		(27)
Unit cell dimensions	nm	Orthorhombic unit cell	$a = 1.06$, $b = 0.54$, $c = 0.51$		(28)
Heat of fusion	kJ mol^{-1}	–	11.3		(29)
			3.28		(30)
			3.59		(31)

† K values can be calculated from expression given for last three entries.

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Degree of crystallinity and density

From density measurements[4]

Polymerization temp. (°C)	Crystallinity (%)	M_n (g mol^{-1})	Density at 20°C (g cm^3)
90	11.3	23,750	1.391
55–60	11.3	75,000	1.391
50	13.2	91,250	1.392
20	15.0	172,250	1.393
−15	57.3	106,300	1.416
−75	84.2	105,300	1.431

From calrimetric measurements[32]

Polymerization temp. (°C)	Crystallinity (%)	M_n (g mol^{-1})
75	18.4	23,2000
65	15.5	38,700
52	15.3	53,500
52	14.4	66,700
25	11.9	136,000
25	11.8	155.000

PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Glass transition temperature	K	Effects of tacticity and molecular weight	–		(33)
		Dilatometry	344		(34)
		DSC, 20°C min^{-1}	371		(35)
		By DSC, 32°C min^{-1}			(36)
		Polymerization temp. (°C)	[η] (ml g^{-1})*		
		90	–	353	
		50	80	358	
		0	108	370	
		−20	103	373	
		−30	125	373	
		−50	–	378	
		−60	90	380	
Melting transition temperature	K	Calorimetry		485-583 473–573 (decomposition)	(31)
Sub-T_g transition temperature	K	Dynamic mechanical		223	(37)

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PROPERTY	UNITS	CONDITIONS	VALUE			REFERENCE
Heat capacity	$kJ\,K^{-1}\,mol^{-1}$	100°C	0.0268			(38)
		300°C	0.0594			
		360°C	0.0911			
		380°C	0.0981			
Tensile modulus	MPa	As a function of polymerization temp. (°C)				
		−196	7,584			(39)
		−120	5,171			(39)
		−75	3,861			(39)
		20	2,964			(39)
		30	3,000			(40)
		40	2,930			(40)
		50	2,427			(40)
		60	1,551			(40)
		70	276			(40)
Tensile strength	MPa	Unplasticized	56.6			(41)
		With 10% dioctylphthalate	55.5			
Elongation	%	Unplasticized	85			(41)
		With 10% dioctylphthalate	104			
Dielectric constant ε'	–		60 Hz	1 kHz	10 kHz	(42, 43)
		25°C	3.50	3.39	3.29	
		40°C	3.51	3.40	3.34	
		60°C	3.70	3.61	3.45	
		80°C	4.25	4.09	3.89	
		90°C	6.30	5.05	4.45	
		100°C	10.30	7.77	5.77	
Dielectric loss factor ε''	–		60 Hz	1 kHz	10 kHz	(42,43)
		25°C	0.110	0.081	0.058	
		40°C	0.116	0.081	0.058	
		60°C	0.125	0.080	0.050	
		80°C	0.172	0.120	0.110	
		90°C	0.410	0.500	0.920	
		100°C	1.20	1.415	1.370	
Permeability coefficient P	$m^3(STP)m\,s^{-1}\,m^{-2}\,Pa^{-1} \times 10^{-9}$	Unplasticized film, 25°C				
		H_2	1.3			(44)
		N_2	0.0089			(44)
		O_2	0.034			(44)
		Ar	0.0086			(44)
		CH_4	0.021			(44)
		NH_3	3.7			(45)
		H_2S	0.14			(45)
		CO_2	0.15			(44)
		H_2O	0.12			(44)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Permeability coefficient P	m^3(STP)m s^{-1} m^{-2} $Pa^{-1} \times 10^{-9}$	Plasticized with tricresyl triphosphate (TCP), 27°C		(46)
		5% TCP, H_2	1.4	
		20% TCP, N_2	1.6	
		31% TCP, O_2	2.1	
		40% TCP, Ar	2.7	
Pyrolyzability	—	Dehydrochlorination rate in N_2	—	(47, 48)
		Polyene propagation on degradation	—	(48)
Weathering	—	Change in molecular weight during weathering	—	(49)

*In cyclohexanone at 25°C.

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Poly(vinyl chloride), head-to-head

MEIFANG QIN

ACRONYMS, TRADE NAMES H-H PVC, HH PVC, Cl-*cis*-PBD, Cl-*trans*-PBD, chlorinated PBD rubber

CLASS Chemical copolymers

STRUCTURE $[-CH_2-CHCl-CHCl-CH_2-]$

MAJOR APPLICATION H-H PVC is mostly studied in academic field to understand its structure/property relationship, thermal degradation behavior, and mechanism. Its properties are compared to those of commercial head-to-tail PVC. Pure H-H PVC has no significant industrial applications. H-H PVCs containing 40–65 wt% of Cl, also called chlorinated polybutadiene rubber-resins, are used for coating, paint-based applications and the preparation of threads, tires, tubings, and films, etc.

PROPERTIES OF SPECIAL INTEREST Preparation methods. Toughness and durability. Good compatibility with other polymers and plasticizers. Tacticity and spectrum properties.

PREPARATIVE TECHNIQUE Chlorination of 1,4-polybutadiene solution at room temperature with molecular chlorine, using solvents that favor ionic reaction such as dichloromethane and chloroform. Pure H-H PVC is made by 1,4-PBD with high *cis* content.[1–8]

PROPERTY	UNITS	CONDITIONS	VALUE					REFERENCE
Tacticity	—	Chlorinated-*trans*-PBD (Cl-*trans*-PBD)	Diisotactic poly(*erythro*-1,2-dichloro butamer)					(6, 10)
		Chlorinated-*cis*-PBD (Cl-*cis*-PBD)	Disyndiotactic poly(*threo*-1,2-dichloro butamer)					
Infrared absorption at fingerprint region	cm^{-1}		Wavenumbers					
		Cl-*cis*-PB	795	725	680	650	590	(2, 7, 8, 12)
		Cl-*trans*-PB	795		686	650		(8, 12)
NMR	ppm		CH_2	CHCl				
		^{13}C	32.9, 33.3	65.7, 66.1				(2, 7, 9)
		^{1}H	8.0	5.8				(2, 7)

Transition temperature of partially chlorinated *cis*-1,4-PBD measured by DMA[2]

Degree of chlorination (%)	β low (K)		α low (K)		β high (K)	
	E''	tan δ	E''	tan δ	E''	tan δ
40	176	178	276	275	321	344
58	173	173	294	294	324	348

Thermal transition temperature of chlorinated *cis*-1,4-PBD measured by DSC

Weight percent of $-CH_2-CHCl-CHCl-CH_2-$ units	Temperature (K)				Reference
	T_g (low)	T_{cr} (low)*	T_m (low)†	T_g (high)	
0	165	203	270	–	(2)
0.40	166	201	267	–	(2)
0.61	165	202	266	324	(2)
0.63	164	209	267	322	(2)
0.72	166	201	266	314	(2)
0.81	162	204	266	337	(2)
0.89	–	–	–	324	(2)
0.91	207	–	–	329	(2)
0.93	–	–	–	326	(2)
1.00	–	–	–	347	(2)
1.00‡	–	–	–	336	(3)

*T_{cr} (low) = crystallization temperature of PB domain.
†T_m (low) = melting temperature of PB domain.
‡Sample made by chlorination of *trans*-1,4-PBD.

Unit cell dimensions[10]

Polymer	Crystal system	Repeat unit per unit cell	Cell dimensions (Å)			Cal. Density ($g\ cm^{-3}$)	Cell angle (degrees)	Space group
			a	*b*	*c*			
Cl-*trans*-PBD	Monoclinic	2	7.05	8.05	5.10	1.46	100	$P2_1/a$
Cl-*cis*-PBD	Monoclinic	2	7.37	5.30	10.10	1.46	134	P2/c

Unperturbed molecular dimension, *K*, and conformational parameter, σ, in different solvents[12]

Sample	Solvent	$K \times 10^3$	σ
Cl-*cis*-PBD	Tetrahydrofuran	1.5	2.3
	Methyl ethyl ketone	2.1	2.5
Cl-*trans*-PBD	Tetrahydrofuran	1.9	2.5
	Dichloroethane	1.6	2.3
PVC	Tetrahydrofuran	3.2	2.9

Conformational population in the chlorinated part of H-HPVC[12]

Sample form	Solvent	Chlorination of *trans*-PBD		Chlorination of *cis*-PBD	
		trans	*gauche*	*trans*	*gauche*
Solution	Tetrahydrofuran	64	35	49	51
Solution	Cyclohexanone	45	55	56	44
Unstretched film	None	63	37	62	38
Stretched film	None	–	–	68	32

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Mark-Houwink parameters: K and $a^{(13)}$

Polymer	Solvent	Temperature (°C)	$K \times 10^4$ (ml g^{-1})	a
Cl-*cis*-PBD	Tetrahydrofuran	30	2.53	0.71
	Methyl ethyl ketone	30	9.46	0.57
Cl-*trans*-PBD	Tetrahydrofuran	30	6.21	0.61
	Dichloroethane	30	9.64	0.54

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Second virial coefficient A_2	mol cm^3 g^{-2}	Polymer/Solvent		(13)
		Cl-*cis*-PBD/tetrahydrofuran	1.0×10^{-3}	
		Cl-*cis*-PBD/methyl ethyl ketone	0.5×10^{-3}	
		Cl-*trans*-PBD/tetrahydrofuran	1.1×10^{-3}	
Stabilities				(4, 11, 14)
Initial decomposition temperature	K	—	463	
Degradation product by thermal volatilization analysis	—	—	HCl, ethylene, propylene, benzene, methane	
Activation energy for dehydrochlorination	kcal mol^{-1}	—	23	

Pyrolysis product in helium at 500°C

Pyrolysis product	Percentage ratio of each peak height to the summation of all peak heights	
	100% chlorinated 98% *cis*-1,4-PBD	100% chlorinated 59% *trans*-1,4, 23% 1,2-, 18% *cis*-1,4-PBD
Aliphatic hydrocarbons	7.40	24.5
Benzene	32.48	34.5
Toluene	6.31	8.6
Ethylbenzene	1.34	3.3
o-Xylene	1.01	1.15
Monochlorobenzene	31.48	3.2
Styrene	2.33	3.1
Vinyltoluene	2.61	0.9
p-Dichlorobenzene	2.12	0.1
o-Dichlorobenzene	3.7	1.7
1,3,5-Trichlorobenzene	0.84	1.13
1,2,4-Trichlorobenzene	0.65	1.65
Naphthalene	3.35	4.3
α-Methylnaphthalene	0.42	2.35
β-Methylnaphthalene	—	1.5

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Poly(vinylferrocene)

IAN MANNERS

CLASS Inorganic and semi-inorganic polymers

STRUCTURE $[CH_2CH\{(C_5H_4)Fe(C_5H_5)\}]_n$

PROPERTIES OF SPECIAL INTEREST Interesting electrical properties.

SYNTHESIS The synthesis of poly(vinylferrocene) can be achieved via the radical induced polymerization of vinylferrocene, $(\eta\text{-}C_5H_4(CH{=}CH_2))Fe(\eta\text{-}C_5H_5)$.(1) Other routes to poly(vinylferrocene) include cationic(2) and anionic(3) initiation, as well as Ziegler–Natta polymeriztion.(2)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
UV-vis absorption, λ_{max}	nm	CH_2Cl_2 solution	440	(4)
UV-vis absorption coefficient, ε	$M^{-1}\,cm^{-1}$	CH_2Cl_2 solution	109	(4)
Glass transition temperature	K	DSC experiment	463	(4)
Melting temperature	K	DSC experiment	554–558	(4)

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Poly(vinyl fluoride)

RONALD E. USCHOLD

ACRONYM, TRADE NAMES PVF, Tedlar® PVF Film, Tedlar® SP Film, PV-116 Resin

CLASS Vinyl polymers

REPEAT UNIT $-(CH_2CHF)_n-$

MAJOR APPLICATIONS As a protective surfacing material for: aircraft interior wall and ceiling panels, architectural fabrics, exterior building panels, wall coverings, reinforced vinyl sheeting for signs and awnings, automotive tubing, thermoformed plastic laminates, truck body panels, solar panels, and greenhouse glazing. As a release sheet for curing: epoxy circuit boards and composite panels.

PROPERTIES OF SPECIAL INTEREST Weathering resistance, antisoiling properties, chemical resistance, UV resistance, and durability.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Preparative techniques	Process			
	Emulsion: 4.0–100 MPa, 46–250°C, water soluble radical initiator, fluorinated surfactant			(1, 2, 3)
	Suspension: 2.5–10 MPa, 25–100°C, monomer soluble radical initiator, water soluble suspending agent			(4, 5)
Molecular weight (of repeat unit)	$g\,mol^{-1}$	$CH_2{=}CHF$	46.04	–
Head-to-head sequences	%	$-CH_2CHFCH_2CHF-$	87–89*	(6, 7)
Monomer inversions	%	$-CH_2CHFCHFCH_2-$	11–13*	(6, 7)
Branch points	%	$-CH_2CF(CH_2CHF-)CH_2CHF-$	0.5–0.7†	(7)
End group	%	$-CH_2CH_2F$	0.2–0.5†	(7)
Tacticity	–	Atactic, Bernoullian distribution	$P_m = 0.43$	(8)
Typical polymer M_w range	$g\,mol^{-1}$	–	1.43–6.54 ($\times 10^5$)	(9)
Typical polydispersity index (M_w/M_n)	–	–	2.5–5.6	(9)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
IR absorption frequencies	cm^{-1}	–	2,940 1,710 1,415 1,370 1,235 1,140 1,090 1,025 890 830 460	(13)
UV/VIS absorption frequencies	cm^{-1}	Transmittance (%)		(13)
		<10	<44,000	
		>80	42,000–25,000	
		>90	25,000–7,000	
NMR signals	ppm	Structure	Chemical Shift	
		$-CH_2CHFCH_2-$	−174 to −184	(6, 7, 10)
		$-CH_2CHFCHFCH_2-$	−188 to −200	(6, 7, 10)
		3°F at branch	−147	(7)
		$-CH_2F$ end group	−220	(7)
Thermal expansion coefficient	K^{-1}	20–100°C, TMA	9×10^{-5}	(13)
Density	$g\,cm^{-3}$	Crystallinity (%)		
		Amorphous	1.36	(10)
		20	1.368	(10)
		22	1.370	(10)
		28	1.375	(10)
		32	1.379	(10)
		37	1.383	(10)
		50	1.395	(10)
		61	1.405	(10)
		100	1.44	(11)
Solvents (above 120°C)	Dimethylacetamide, dimethylformamide, N-methyl pyrrolidone, γ-butyrolactone			(13)
Nonsolvents	Alcohols, ketones, esters, ethers, aliphatics, aromatics			(13)
Solubility parameter	$(Pa)^{1/2}$	–	~25	(13)
Mark-Houwink parameters: *K* and *a*	$K = ml\,g^{-1}$ a = None	DMF at 90°C	$K = 6.52 \times 10^{-5}$ $a = 0.8$	(9)

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Poly(vinyl fluoride)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Crystalline state properties				(11)
Lattice	–	–	Hexagonal	
Unit cell dimensions	Å	–	$a = b = 4.93$, $c = 2.53$	
Unit cell angles	Degrees	–	$\alpha = \beta = 90$, $\gamma = 120$	
Degree of crystallinity	%	Drawn at 90°C, annealed at 140°C	37	
Glass transition temperature	K	DMA, 1 Hz	337	(13)
Melting point (DSC)	K	Commercial resin	463–466	(13)
		37% crystallinity	470–478	(12)
		45% crystallinity	491–498	(12)
		50% crystallinity	498–508	(12)
Softening point	K	DMA, 1 Hz	398–403	(13)
Tensile modulus	MPa	ASTM D882-80		(14)
		Unoriented, unpigmented film	1,170	
		Oriented, unpigmented film	2,300	
Tensile strength	MPa	ASTM D882-80		(14)
		Unoriented, unpigmented film	34	
		Oriented, unpigmented film	83	
Ultimate elongation	%	ASTM D882-80		(14)
		Unoriented, unpigmented film	175	
		Oriented, unpigmented film	100	
Yield strain	%	ASTM D882-80		(14)
		Unoriented, unpigmented film	4	
		Oriented, unpigmented film	2	
Yield stress	MPa	ASTM D882-80		(14)
		Unoriented, unpigmented film	23	
		Oriented, unpigmented film	48	
Storage modulus	MPa	Unoriented, unpigmented film		(13)
		25°C, 1 Hz	2,000	
		75°C, 1 Hz	400	
		150°C, 1 Hz	50	
Loss modulus	MPa	Unoriented, unpigmented film		(13)
		25°C, 1 Hz	16	
		75°C, 1 Hz	60	
		150°C, 1 Hz	100	
Index of refraction	–	–	1.46	(14)
Dielectric constant	–	1 kHz at 22°C	8.5	(14)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Dielectric strength	$V\ \mu m^{-1}$	60 Hz	135	(14)
Corona endurance	h	60 Hz, 40 $V\ \mu m^{-1}$	2.5–6	(14)
Dissipation factor	%	1,000 Hz, 22°C	1.6	(14)
		1,000 Hz, 70°C	2.7	
		10 kHz, 22°C	4.2	
		10 kHz, 70°C	2.1	
Volume resistivity	ohm cm	22°C	4×10^{13}	(14)
		100°C	2×10^{10}	
Surface tension	$mN\ m^{-1}$	Contact angle	38	(13)
Coefficient of friction	–	PVF to PVF, 23°C	0.24	(13)
		PVF to steel, 23°C	0.13	
Maximum use temperature	K	Continuous	380	(14)
		1–2 h	475	
Decomposition temperature	K	Air	525	(14)
Chemical resistance	–	Acids, bases, solvents 1 yr, 25°C	No visible effect	(14)
		Acids, bases, solvents 2 h boiling	No visible effect	
		Soil burial, 5 yr	No visible effect	
Weatherability	–	5 yr Florida exposure facing south, 45° from horizontal	Excellent	(14)
Gas permeability	$nmol\ m^{-1}\ s^{-1}\ GPa^{-1}$	25 mm film, 23°C, 98 kPa		(14)
		Carbon dioxide	22.4	
		Helium	302	
		Hydrogen	117	
		Nitrogen	0.5	
		Oxygen	6.6	
Vapor permeability	$nmol\ m^{-2}\ s^{-1}$	Solvent partial pressure at 23°C		(14)
		Acetic acid	4.9	
		Acetone	1,570	
		Benzene	13	
		Carbon tetrachloride	3.9	
		Ethyl acetate	138	
		Hexane	10	
		Water (39.5°C)	22	

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Poly(vinyl fluoride)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Availability	—	Standard and custom colors	12–75 μm film up to 3 m wide	—
Cost	US$ m^{-2}	Depends on type and color; $5,000 minimum order	1–5	—
Supplier	DuPont Co., 1007 Market Street, Wilmington, Delaware 19898. (800) 441-7515			—

*Percent monomer units.
†Percent fluorine atoms.

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Poly(vinylidene chloride)

ANTHONY L. ANDRADY

ACRONYM, TRADE NAME PVDC, Saran (copolymer)

CLASS Vinylidene polymers

STRUCTURE $[-CH_2CCl_2-]$

MAJOR APPLICATIONS Homopolymer and copolymers—usually with vinyl chloride (VC), or methyl acrylate (MA)—used in solvent-based or latex barrier coatings on cellophane, paperboard, plastic film, and rigid food containers. Films of copolymer used as household cling wrap. Also used with other polymers in multilayer barrier films or containers mostly in packaging applications. Also used in fibers and adhesives.

PROPERTIES OF SPECIAL INTEREST Exceptional barrier properties with very low oxygen and water vapor permeability.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Preparative techniques	Radical polymerization:			
	Photochemical initiation with UV lamp			(1)
	Aqueous emulsion (redox initiators), 32°C			(2)
	Suspension (peroxide initiators)			(3)
Typical comonomers	Vinyl chloride (5–40%)			(4)
Molecular weight (of repeat unit)	$g\,mol^{-1}$	—	96.95	—
Head-to-head content	%	—	> 1	(5, 6)
Molecular weight range	$g\,mol^{-1}$	—	DP = 100–10,000	(7)
Polydispersity	—	—	1.5–2.0	(8)
NMR	15% solution in hexamethylphosphoramide, 40°C			(9)
Solvents	THF (hot), tetralin (hot), trichloroethane 1,2 dichlorobenzene, dioxane, DMF, cyclohexanone, butyl acetate, cycloheptanone cyclooctanone, N-acetylpiperidine, N-methyl pyrolidinone, trimethylene sulfide			(10–14)
Nonsolvents	Hydrocarbons, chloroform, alcohols, phenol, THF, carbon disulfide			—

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Mark-Houwink parameters: K and a	$K = \text{ml g}^{-1}$ a = None		$K \times 10^3$	a	
		1-Methyl-2-pyrrolidinone, 25°C	13.1	0.69	(15)
		Tetramethylene sulfoxide, 25°C	13.9	0.69	(15)
		Hexamethylenephosphoramide, 25°C	25.8	0.65	(16)
Unit cell dimensions	Å	Mono	$a = 13.69$, $b = 4.67$, $c = 6.296$		(17)
			$a = 22.54$, $b = 4.68$, $c = 12.53$		(18)
Heat of fusion	kJ mol^{-1}	At melting point	5.623		(19)
			4.60–7.95		(16)
Entropy of fusion	kJ mol^{-1}	–	0.0120		–
Density (crystalline)	g cm^3	Volumetry during polymerization	1.97		(20)
			1.80–1.97		(16)
			1.948		(17)
			1.958		(18)
Density (amorphous)	g cm^3	–	1.775		(16)
		Molding resin grade	1.65–1.72		
Glass transition temperature	K	Dynamic-mechanical	255		(19, 21)
		Dilatometry	255–258		(2, 21)
		Calorimetry	255		(22)
Melting transition temperature	K	Calorimetry	468		(23)
			471–478		(24)
			473–508		(22)
Sub-T_g transitions	K	β transition	285		(25)
Heat capacity	$\text{kJ K}^{-1}\text{ mol}^{-1}$	100°C	0.0363		(26)
		200°C	0.0575		
		250°C	0.0690		
Tensile modulus	MPa	Machine direction	483		(27)
		Transverse direction	34.5		
Yield strength	MPa	Machine direction	69		(27)
		VD-VC molding resin grade	19.3–36.2		(16)
Tensile strength	MPa	Machine direction	73		(27)
		VD-VC molding resin grade	24.1–34.5		(26)
		Transverse direction	110		–

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PROPERTY	UNITS	CONDITIONS		VALUE	REFERENCE
Elongation	%	Machine direction		55	(27)
		Transverse direction		35	—
		VD-VC molding resin grade		160–240	(16)
Impact strength, Izod	$J\,m^{-1}$	VD-VC molding resin grade (of notch)		21.35–53.38	(16)
Hardness	Rockwell M	—		50–65	(16)
Permeability coefficient P	$m^3(STP)m\,s^{-1}\,m^{-2}\,Pa^{-1}$ ($\times 10^{-9}$)	Temp (°C)	Gas		
		30	N_2	0.000706	(28)
		30	O_2	0.00383	(28)
		30	CO_2	0.0218	(28)
		25	H_2O	7.0	(29)
Pyrolyzability	—	120–190°C		Only HCL given off (up to 60% available Cl)	(30)

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Poly(vinylidene fluoride)

JERRY I. SCHEINBEIM

ACRONYMS, TRADE NAMES PVDF, PVF2, Kynar, Solef, Neoflon, Foraflon, KF, Soltex

CLASS Vinylidene polymers

STRUCTURE $-(CH_2CF_2)_n-$

MAJOR APPLICATIONS Wire and cable insulation, tubing, piping, sheet and melt-cast films for electrical and electronics, binder for high-quality metal finishes for building components used on exterior wall panels, roofing shingles, and on industrial, commercial and residential buildings, used in fluid handling systems for solid and lined pipes, fittings, valves, and pumps, in manufacture of microporous and ultrafiltration membranes, chemical-tank lining, telephone headset, infrared sensing, hydrophones, keyboards and, printers.

PROPERTIES OF SPECIAL INTEREST Excellent mechanical properties and resistance to severe environmental stress, good chemical resistance, good piezoelectric and pyroelectric properties

PREPARATIVE TECHNIQUES Emulsion polymerization: (a) 300–800 psig, perfluorinated surfactant initiator, 65–85°C, 2–6 h;[1] (b) 200 lb in^2, 50–110°C, fluorinated surfactant, 17–21 h, iron powder.[2]

Suspension polymerization: suspending agent, reaction accelerator, water soluble initiator, 300–1,000 psig, 35–100°C.[3]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Monomer and molecular weight	g mol^{-1}	$CH_2=CF_2$	64.034	—
Head-to-head sequences	%	$CF_2-CF_2-CH_2-CH_2$	3.5–6	(4–6)
Typical molecular weight range	g mol^{-1}	—	$3.4–40 \times 10^4$	(7)
Typical polydispersity index	—	—	1.62–2.14	(7)
Tacticity	% Isoregic	—	95–97	(8)
Morphology (crystal forms)	—	—	α, β, γ, δ	—
IR (characteristic absorption frequency)	cm^{-1}	α form	530	(9, 10)
			615	(9)
			764	(9)
			796	(9)
		β form	442	(9)
			470	(9)
			484	(9)
			510	(9)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
IR (characteristic absorption frequency)	cm^{-1}	γ form	430	(9)
			481	(9)
NMR	–	–	–	(11–15)
Crystal form/density	$g\,cm^{-3}$	α form	1.92	(8, 16)
		β form	1.8	(8)
		Amorphous	1.68	(16)
Density (crystalline)	$g\,cm^{-3}$	Molded at 170°C (quenched to 0°C)	1.75–1.78 (47%)	(17)
		Molded at 170°C (quenched to room temperature)	1.779 (60%)	(18)
		Molded at 170°C (quenched to 0°C)	1.768 (65%)	(18)
		Annealed at 120°C for one day	1.769 (69%)	(18)
Thermal coefficient of linear expansion	K^{-1}	–	0.7–1.5 ($\times 10^{-4}$)	(19)
Thermal conductivity	$W\,m^{-1}\,K^{-1}$	25–160°C	0.17–0.19	(19)
Compressive strength	MPa	At 25°C	55–90	(19)
Solvents	–	–	Acetone, benzaldehyde, DMF, THF	(20)
		Above 60°C	Acetophenone	(7)
		25°C	DMA	(7)
		150–190°C	Benzophenone	(7)
Nonsolvents	–	–	Acetic acid, benzyl alcohol, 1,2-dibromoethane, ethanol	(21)
Solubility parameters	MPa	DMA	16.8	(21)
		DMF	17.4	
		DMSO	18.4	
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None	DMA	$K = 17.8 \times 10^{-6}$, $a = -0.74$	(22)
		DMF	$K = 31.7 \times 10^{-6}$, $a = -0.70$	(22)
		NMP	$K = 48.8 \times 10^{-6}$, $a = -0.68$	(22)
		Acetophenone, 85°C	$K = 2.13 \times 10^{-4}$, $a = 0.62$	(7)
		Benzophenone, 165°C	$K = 13.6 \times 10^{-4}$, $a = 0.44$	(7)
		Benzophenone, 180°C	$K = 7.54 \times 10^{-4}$, $a = 0.49$	(7)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Second virial coefficient	$cm^3 g^{-2} mol$	Acetophenone, 85°C	0.3–7.6 ($\times 10^{-4}$)	(7)
Root-mean-square radius of gyration	–	DMA	$29.5M_w^{0.55}$	(22)
		DMF	$813M_w^{0.51}$	
		NMP	$28.2M_w^{0.45}$	
Unit cell dimensions			Unit cell angles	(16, 23)
Form I (β)	Å	Lattice = orthorhombic; space group = Cm2m-$C_{2\nu}^{14}$	$a = 8.58$, $b = 4.91$, $c = 2.56$	
Form II (α)	Å	Lattice = monoclinic; space group = $P2_1$/c-C_{2h}^{5}	$a = 4.96$, $b = 9.64$, $c = 4.62$	
	Degrees		$\beta = 90$	
Form III (γ)	Å	Lattice = orthorhombic; space group = C2cm	$a = 4.97$, $b = 9.66$, $c = 9.66$	(24, 25)
	Degrees		$\gamma = 91$	
Form IV (δ)	Å	Lattice = orthorhombic; space group = P2cn	$a = 4.96$, $b = 9.64$, $c = 4.62$	(24, 25)
Degree of crystallinity	%	–	50	(16, 20)
Heat of fusion	$J g^{-1}$	–	30.5	(9)
		Draw ratio of 4	41.4	

Avrami exponent[26]

Crystallization temp. (K)	Avrami exponent	Kinetic rate constant ($min^{-3.94}$)	Half-time of conversion $t^{1/2}$ (min)
407	3.82	0.49	1.09
409	4.62	0.03	2.15
412	3.62	0.02	2.6
414	4.6	87×10^{-5}	5.45
417	3.3	44×10^{-6}	11.60
419	4.35	46×10^{-7}	20.60
420	2.99	10×10^{-7}	30.00
422	4.23	15×10^{-8}	49.00

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melting point	K	Depends on polymorph	443–473	(8)
			451 (DSC)	(23)
		Oriented PVF2 film (β crystal)	439	(23)
Glass transition temperature	K	–	238	(23)
Other transition temperatures (DMS, DSC) (relaxation)	K	(α_2)	323	(27)
		(α_1)	373	
		(β)	235	
		(γ)	203	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Elastic modulus	$GN\,m^{-3}$	β phase	1–3	(8)
Acoustic impedance	$Gg\,m^{-2}\,s^{-1}$	β phase	2–3	(8)
Tensile strength (ultimate elongation)	(%)	$190\,kg\,mm^{-2}$ fiber, 59% crystallization, crystal melting point = 184°C	22	(28)
		42–58 MPa (homopolymer) (25°C)	50–300	(19)
		34.5 MPa (100°C)	200–500	(19)
Tensile yield strength	MPa	Commercial grade	42.8	(29)
Ultimate tensile strength	MPa	Commercial grade	43.8	(29)
Tensile modulus	MPa	Commercial grade	1,194.4	(29)
Elongation at break	%	Commercial grade	43	(29)
Yield point	MPa	At 25°C	38–52	(19)
		At 100°C	17	
Elastic modulus	$MPa \times 10^3$	At 25°C		(19)
		Tensile modulus	1.0–2.3	
		Flexure modulus	1.1–2.5	
		Compression modulus	1.0–2.3	
Abrasion resistance	–	Tabor CS-17, 0.5 kg load, mg $(1{,}000\ \text{cycles})^{-1}$	17.6	(19)
Index of refraction	–	–	1.42	(19)
Dielectric constant	–	At 25°C		(19)
		60 Hz	9–10	
		103 Hz	8–9	
		106 Hz	8–9	
		109 Hz	3–4	
Dissipation factor	%	–	3–5	(19)
			5–2	
			3–5	
			9–11	
Volume resistivity	–	–	2×10^{12}	(19)
Dielectric strength	$V/(2.54 \times 10^{-5})$	0.003175 m thickness	260	(19)
		0.000203 m thickness	1,300	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Piezoelectric coefficient	cgs esu	α phase, 38% crystallinity poled at 140°C	0.32×10^{-7}	(30)
	pC/N	β phase	20–30	(8)
	pC/N	δ phase	2–3	(8)
Pyroelectric coefficient	$\mu C\, km^{-2}$	β phase	30–40	(8)
Optical transmittance	–	Visible/UV	–	(17)
Specular transmittance	%	At 0.5° cone	85–90	(17)
Coefficient of friction	–	PVF2 to steel	0.14–0.17	(19)
Contact angle	Degrees	Water	82	(31)
		Methylene oxide	63	
		Formaldehyde	59	
		α-Bromonaphthalene	42	
		Glycerol	75	
		Tricresyl phosphate	28	
Solid surface tension	–	Harmonic means	37.4	(31)
		Geometric means	36.2	
		Critical surface tension	36.5	
		Equation of state	25	
Thermal decomposition	Degrees	–	390	(19)
		Charring	480	
Chemical resistance	–	Inorganic acids	No effect	(19)
		Halogens	No effect	(19)
		Oxidants	No effect	(19)
		Weak bases	No effect	(19)
		Aliphatic, aromatic and chlorinated solvents	No effect	(19)
		Strong bases	Softening	(19)
		Amines, esters, and ketones	Swelling and dissolution	(19)
		Acetone (30 min at room temperature)	Etching	(32)
Water absorption	%	–	0.04	(19)
Flammability	–	–	Low to none	–
Flame propagation rate	$ft\ (20\ min)^{-1}$	Maximum flame spread	2.0	(33)
Intrinsic viscosity	–	Commercial grade, 35% crystallinity, melting point 160°C	1.40–1.43	(29)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Viscosity	$dl\,g^{-1}$	DMA NMP DMF DMSO	1.29 1.28 1.17 1.05	(21)
Melt viscosity	poise	Commercial grade, 250°C, shear rate = $10^3\,s^{-1}$	62×10^2	(29)
Moisture vapor permeability	$g\,day^{-1}\,m^{-2}$	1 mm thickness	2.5×10^{-2}	(19)
Gas permeability	cm^3(STP)/(cm s mmHg)	Argon, 25°C, 5.21×10^{-3} cm thickness	$2 \times 10^{-1}2$	(34)
Diffusivity	$cm^2\,s^{-1}$	Argon, 25°C, 5.21×10^{-3} cm thickness	4×10^{-9}	(34)
Cost	kg^{-1} m^{-3}	– –	14.05–14.09 25,270–25,520	–
Suppliers and trademarks		Atochem, France Daikin Kogyo Co., Japan Kureha Chemical Co., Japan Pennwalt Corporation, USA Solvay and Cie, Belgium	Foraflon Neoflon KF Kynar Solef/Vidar	(19)

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Poly(vinyl methyl ether)

JIANYE WEN

ACRONYMS, TRADE NAMES PVME, PVM, Lutonal M, Gantrez M

CLASS Vinyl polymers

STRUCTURE $[-CH_2-\underset{\large OCH_3}{\underset{|}{C}}H-]$

MAJOR APPLICATIONS Plasticizer for coatings; aqueous tackifier; adhesion promoter of nonadhering materials to glass, metal, and plastics; copolymers used in pharmaceuticals; lens arrays for optical device (as thermographic copying material).

PROPERTIES OF SPECIAL INTEREST Viscous and balsamlike; high adhesion to high and low surface-energy free substrates.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Bulk density	$g\,cm^{-3}$	Gantrez M-154†	1.03	(1)
		Gantrez M-574†	0.96	(1)
		Gantrez M-555†	0.94	(1)
		Gantrez M-550†	0.94	(1)
		20°C	1.0580	(2)
		40°C	1.0436	(2)
		60°C	1.0294	(2)
		80°C	1.0152	(2)
		100°C	1.0011	(2)
		120°C	0.9871	(2)
		25–120°C	$1.725 - (7.259 \times 10^{-4})T + (0.116 \times 10-6)T^2$	(2)
Coefficient of thermal expansion	K^{-1} $(\times 10^{-4})$	40°C	6.87	(2)
		60°C	6.92	
		80°C	6.96	
		100°C	7.01	
		120°C	7.06	

Crystallographic data[3,4]

System	Crystal space group	Unit cell parameter *a*	*b*	*c*	Density ($g\,cm^{-3}$)	Chain conf. N^*P/Q
RHO	D3D-6	16.20	16.20	6.50	1.175	2*3/1
RHO	D3D-6	16.25	16.25	6.50	1.168	2*3/1

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Flash point	K	Gantrez M-154†	–	(1)
		Gantrez M-574†	295	
		Gantrez M-555†	295	
		Gantrez M-550†	295	
Glass transition temperature T_g	K	–	239	(5)
			242	(6)
Isothermal compressibilities	bar^{-1} ($\times 10^{-5}$)	20°C	5.3	(7)
		40°C	5.8	
		60°C	6.4	
		80°C	7.2	
		100°C	8.1	
		120°C	9.2	

Mark-Houwink parameters: K and a[8]

Solvent	Temp. (°C)	Mol. wt. range ($M \times 10^4$)	$K \times 10^3$ ($ml\,g^{-1}$)	a
Benzene	30	–45	76	0.60
Butanone	30	–45	137	0.56

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melting temperature T_m	K	–	417	(5)
			417–387	(3)
Refractive index n_D	–	30°C, isotactic	1.4700	(9)
Solvent	Water, toluene, halogenated hydrocarbons, benzene, *n*-butanol, methyl ethyl ketone, ketone, ethanol, acetone, ethylacetate, water (cold)			(1, 10)
Nonsolvents	Heptane, ethylene glycol, ethyl ether, water (hot), (methanol, acetone, and water for crystalline polymer)			(10)
Specific viscosity η_{sp}	1 g in 100 ml	Gantrez M-154†	0.47	(1)
		Gantrez M-555†	0.77	
		Lutonal M‡	0.68	
Surface tension	$mN\,m^{-1}$	$M_n = 46{,}500$, $M_w = 99{,}000$		(11)
		20°C	31.8	
		150°C	22.1	
		200°C	18.3	
	$mN\,m^{-1}\,K^{-1}$	$-d\gamma/dT$	0.075	
Viscosity	p	Gantrez M-555†	~15	(1)
		Gantrez M-574†	~30	
		Gantrez M-154†	~40	

†Product of GAF Corp.
‡Product of BASF Corp.

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Poly(vinyl methyl ether)

Unperturbed dimension*(12, 13)

Conditions	$r_o/M^{1/2} \times 10^4$ (nm)	$r_{of}/M^{1/2} \times 10^4$ (nm)	$\sigma = r_o/r_{of}$	$C_\infty = r_{o2}/nl^2$
Benzene; butanone; 30°C	900 ± 30	404	2.23 ± 0.13	9.95

*See reference (12) for details.

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Poly(vinylmethylsiloxanes), cyclic

STEPHEN J. CLARSON

ACRONYM Cyclic PVMS

CLASS Cyclic polymers

STRUCTURE $-[(CH_2{=}CH)(CH_3)SiO]_x-$

INTRODUCTION Cyclic poly(vinylmethylsiloxanes) are an interesting cyclic polymer system because they contain a reactive pendent group. Thus, possible chemistries include hydrogenation, which yields cyclic poly(ethylmethylsiloxane), that is, $-[(CH_3CH_2)(CH_3)SiO]_x-$. This route has also been used to deuterate the rings for neutron scattering investigations, that is, $-[(CH_3CHD)(CH_2D)SiO]_x-$. Other useful reactions are with molecules containing terminal or pendent Si–H groups, which can readily be attached by hydrosilation chemistry. This functional ring system also shows that one can directly prepare elastomeric network structures having none of the usual network defects (e.g., dangling chain ends, etc.). Although there are a limited number of studies of these novel functional rings to date, the large rings have been successfully isolated from ring-chain equilibration reactions carried out in solution. Following fractionation, some investigations of the physical properties of these cyclic polymers have be carried out and have also been compared with their linear polymer analogs.

MAJOR APPLICATIONS Ring-opening polymerization of small rings to give linear PVMS high polymers. Copolymerization with other siloxane small rings to give copolymers of controlled composition. Both the homopolymer and copolymers are widely used for preparing silicone elastomers.

PROPERTIES OF SPECIAL INTEREST Viscous fluids having good thermal stability.

PREPARATIVE TECHNIQUES Ring-chain equilibration reactions.[1,2]

Selected properties of the cyclic polymers (r) compared to linear poly(vinylmethylsiloxanes) (l)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Characteristic ratio $\langle r^2\rangle/nl^2$	–	Derived from molar cyclization equilibrium constants in 50% toluene solution at 383 K	7.8	(2)
Intrinsic viscosities $[\eta]_r/[\eta]_l$	–	In toluene at 298 K	0.69	(1–3)
Density	$kg\,m^{-3}$	At 298 K; $M_n = 5{,}430\,g\,mol^{-1}$; and $M_w/M_n = 1.06$	1,006.0	(1, 2)
Refractive index	–	589.3 nm		(1, 2)
		$M_n = 5{,}430\,g\,mol^1$; $M_w/M_n = 1.06$		
		At 298 K	1.4458	
		At 303 K	1.4421	
		At 313 K	1.4380	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Refractive index	–	589.3 nm		(1, 2)
		$M_n = 11{,}440$ g mol^{1}; $M_w/M_n = 1.14$		
		At 298 K	1.4465	
		At 303 K	1.4427	
		At 313 K	1.4385	
Glass transition temperature T_g	K	$M_n = 5{,}430$ g mol^{1}; $M_w/M_n = 1.06$	144.5	(1, 2)
		$M_n = 11{,}440$ g mol^{1}; $M_w/M_n = 1.14$	144.7	
Melt viscosity	kg m^{-1} s^{-1}	$10^3\eta$ at 298 K; $M_n = 5{,}430$ g mol^{1}; $M_w/M_n = 1.06$	75.9	(1, 2)
Activation energy	kJ	For viscous flow; $M_n = 5{,}430$ g mol^{1}; $M_w/M_n = 1.06$	16.75	(1, 2)

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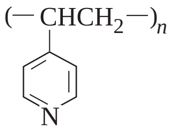
Poly(4-vinyl pyridine)

JOHN H. KO

ACRONYMS, TRADE NAME PVP, P4VP, Reillex®

CLASS Vinyl polymers; homopolymers

STRUCTURE



MAJOR APPLICATIONS Poly (4-vinylpyridine) (P4VP) with its nucleophilic and weakly basic ring nitrogen has found uses in the areas of metal recovery (complex), and pollution control for removal of acidic and neutral materials. It is also used as an acid scavenger and catalyst and catalyst support. Commercial resin beads are mostly prepared by suspension polymerization with cross-linker such as divinylbenzene.[1,2]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Basicity, pKa	—	45% ethanol/55% water	3.25	(3)
Glass transition temperature	K	P4VP P2VP	~ 415 357	(4)
Density	$g\,cm^{-3}$	At 20°C	1.114	(4)
Melting point	K	DSC, isotactic P2VP crystallized at 130°C	450, 472.5 (two peaks)	(5)
Heat of fusion	$kJ\,mol^{-1}$	Isotactic P2VP	02.07	(5)
Dielectric constant	—	10 kHz, 50 K	2.88	(6)
Suppliers	Aldrich Chemical Co., 1001 West St. Paul Avenue, Milwaukee, WI 53233, USA Poly(4-vinylpyridine), 2% or 25% cross-linked Reilly Chemicals, SA, Rue Defacqz 115, Boite 19, B-1050 Brussels, Belgium Reillex® cross-linked poly(4-vinylpyridine) polymers			

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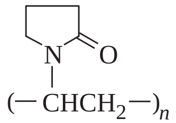
Poly(N-vinyl pyrrolidone)

JOHN H. KO

ACRONYM, ALTERNATE NAMES, TRADE NAMES PVP, povidone, crospovidone, Luviskol®, Kollidon®, Divergan®, Plasdone®, Biodone®, Polyclar®, Albigen®, Peregal®

CLASS Vinyl polymers; homopolymers

STRUCTURE



MAJOR APPLICATIONS Additives (clarifying agent, stabilizing agent, viscosity modifier); adhesives; agriculture; coatings (paints and surface coatings, inks, paper, printing); cosmetics (detergent, soap, hair spraying agent, dye); medical devices (ophthalmic, lubricious coating, biocompatibility coating, complex); pharmaceuticals (control release, binder, stabilizer for polymerization, thickener); photography.

PROPERTIES OF SPECIAL INTEREST PVP powder is white, stable, hygroscopic and water soluble. Forms complexes with many substances.[1,2,3] Coated PVP solution forms brittle, clear, and glassy films.

PROPERTY	UNITS	CONDITIONS	VALUE			REFERENCE
Solubility	%	Soluble	>10			(4)
		Insoluble	<1			
Solvents	Water, alcohol (methanol, ethanol, propanol, butanol, glycol); ester alcohol (ethylene glycol monoethylether, diethylene glycol, polyethylene glycol, 1,4-butanediol); chlorinated hydrocarbon (dichloromethane, chloroform); amine (butylamine, ethylenediamine); acid (formic, acetic, propionic); dilute acid, base, low salt solutions					
Nonsolvents	Hydrocarbons (benzene, hexane, pentane, cyclohexane, toluene, xylene, mineral oil); ethers (dioxane, diethyl ether, ethyl vinylether); ketones (acetone, cyclohexanone); esters (ethyl acetate, methyl acetate); chlorinated hydrocarbons (carbon tetrachloride, chlorobenzene)					
K-value	—		M_w	M_n	M_v	(4, 5)
		17	9×10^3	2.5×10^3	9.2×10^3	
		30	4.5×10^3	1×10^4	4×10^4	
		60	3.5×10^5	9×10^4	3×10^5	
		80	9×10^5	2.85×10^5	6×10^5	
		90	1.2×10^6	3.6×10^5	1.1×10^6	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Coil dimension (end-to-end distance)	nm	In 0.9% NaCl		(5)
		K = 12	2.2	
		K = 17	5	
		K = 20	7	
		K = 90	100	
pH	–	5% in water	3–7	(3, 4)
Theta temperature	K	$M_n = 3.26 \times 10^5$		(6)
		0.55M Na_2SO_4/water	301	
		Water	297	
		2-Propanol	297	
Second virial coefficient	$mol\,cm^3\,g^{-2}$	Osmotic pressure in 2-propanol		(6)
		$M_n = 3.26 \times 10^{5*}$	0.58	
		$M_n = 1.68 \times 10^5$	0.63	
		$M_n = 0.99 \times 10^5$	0.78	
Mark-Houwink parameter: *a*	–	Water	0.82	(6)
Heat of solution	$kJ\,mol^{-1}$	Water	−16.6	(6)
		0.2 molal Na_2SO_4/water	−11.6	
Glass transition temperature	K	DSC, M_w = light scattering		(4)
		$M_w = 9 \times 10^{3*}$	382	
		$M_w = 4.5 \times 10^4$	448	
		$M_w = 3.5 \times 10^5$	449	
		$M_w = 9 \times 10^5$	452	
		$M_w = 1.2 \times 10^6$	452	
		$M_v = 7.5 \times 10^{5*}$		(7, 8)
		Water content		
		0%	448	
		2%	427	
		8%	368	
		16%	318	
		Cross-linked PVP (Crospovidone)	463–468	(5)
Density	$g\,cm^{-3}$	25°C	1.25	(9)
Diffusion coefficient	$cm^2\,s^{-1}$	Electrophoresis	4.81×10^{-7}	(10)
Index of refraction n_D	–	At 25°C	1.53	(9)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Index of refraction n	—	Ultrasonic at 30°C		(11)
		Concentration (in water)		
		0.000875 mol l^{-1}	1.339	
		0.001500 mol l^{-1}	1.343	
		0.004000 mol l^{-1}	1.357	
Suppliers	BASF Corp., 100 Cherry Hill Road, Parsippany, NJ 07054, USA ISP, 1361 Alps Road, Wayne, NJ 07470, USA			

* M_w: light scattering; M_n: osmometry; M_v: viscometer.

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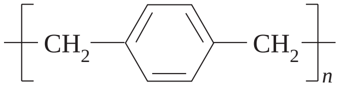
Poly(*p*-xylylene)

SHRISH RANE AND GREG BEAUCAGE

ACRONYM, TRADE NAME PPX, Parylene N (Union Carbide)

CLASS Polyaromatics

STRUCTURE



MAJOR APPLICATIONS Films and coatings on electronic components; insulating applications.

SPECIAL PROPERTIES High thermal stability; excellent barrier and dielectric properties; high resistance to electronic irradiation.

SYNTHESIS[1–5]

(a) Pyrolitic decomposition polymerization of cyclic di-*p*-xylylene.
(b) Plasma decomposition of cyclic di-*p*-xylylene.
(c) Vapor phase pyrolysis of di-*p*-xylylene or diesters of α,α'-dihydroxy-1,4-xylylenes or α,α'-dibromo-1,4-xylylenes in the presence of Zn/Cu.
(d) Electrochemical polymerization of α,α'-dibromo-1,4-xylylene in DMF and tetra-ethyl-ammonium-bromide (TEAB) as the electrolyte.
(e) By the ''Wessling Process'': heating high molecular weight water soluble precursor polyelectrolyte (α,α'-bis-tetrahydrothiophenium chloride)-pxylylene with NaOH.

IR properties[5,6]

Values of ν (cm^{-1})	Types of vibrations
3,150; 3,110; 3,060; 3,030; 2,995	C–H stretch of aromatic ring
2,950; 2,935; 2,870	Asymmetrical and symmetrical C–H stretch of $-CH_2-$
1,900; 1,795	Characteristic bands for a 1,4, substituted aromatic ring
1,497; 1,350	Deformation of C–H from $-CH_2-$
1,210; 1,142; 1,080; 1,021	Planar vibration of C–H from aromatic ring
820	Extra planar vibration of C–H from aromatic ring
540	Extra planar vibration of C–C from aromatic ring

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Poly(*p*-xylylene)

Morphology[1,3,7,8]

PPX	Morphology	Lamellar width (nm)	Lamellar thickness (nm)	Comments
Fiber	Main fiber is made of secondary fibrils	~500 (fibril width)	~10 (fibril thickness)	Low-magnification electron microscopy
Fiber	Shish-Kebab	~100	~25	High-magnification electron microscopy
Melt cryst. films	Spherulitic	—	~8	—
Soln. grown	Lamellae	—	~12	—

Crystal structure

Unit cell type	Unit cell dimensions (nm)			
	a	*b*	*c* (fiber axis)	
α-Monoclinic	0.592	1.064	0.655	$\beta = 134.7^\circ$
β-Trigonal	2.052	2.052	0.655	$\gamma = 120^\circ$

$\alpha \xrightarrow[231^\circ C]{} \beta_1$ condis crystal $\xrightarrow[287^\circ C]{} \beta_2$ condis crystal $\xrightarrow[427^\circ C]{}$ Melt

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Degree of crystallinity X_c	%	—	$35 \sim 66$	—
Chains per unit cell	—	—	2	—
Packing density ρ	$g\,cm^{-3}$	—	0.705	—
Solubility	Generally, PPX is insoluble in most organic solvents. Phenyl derivatives such as phenyl substituted PPX is found to be soluble in common solvents like THF and $CHCl_3$.			(5)
Dielectric loss, tan δ	—	At 1 KHz	1.5×10^{-4}	(9)
Glass transition temperature T_g	K	—	286	(8, 10)
Crystalline melting temperature T_m	K	—	700	(8, 10)
Young's modulus E	MPa	Isotropic film Oriented film Fibers	600–1,400 90,000–100,000 102,000	(1, 4, 8, 10)
Tensile stress σ	MPa	Isotropic film Oriented film Fibers	25–62 1,800 3,000	(1, 4, 8, 10)
Elongation at break	%	Isotropic film Oriented film Fibers	18–330 — —	(1, 4, 8, 10)

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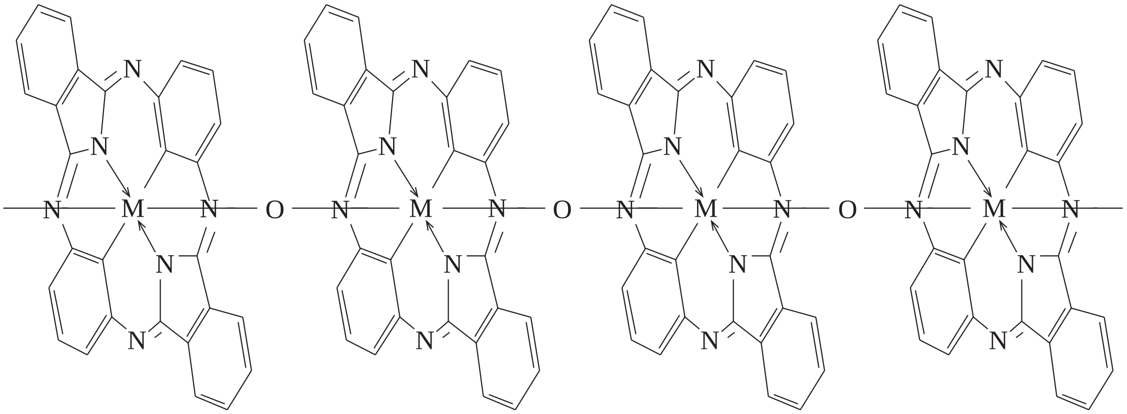
Silicon (germanium) oxo hemiporphyrazine polymers

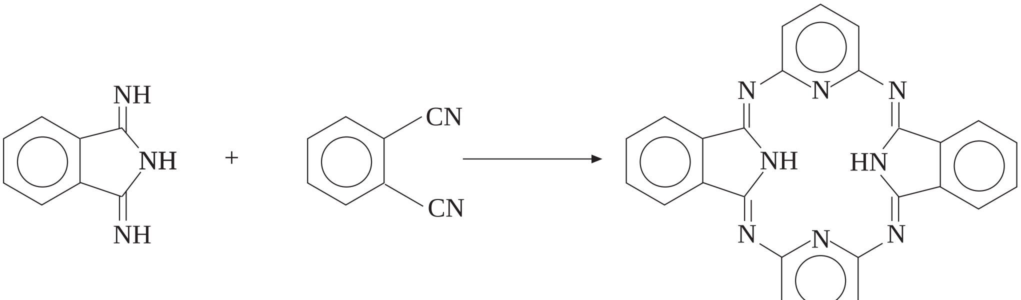
MARTEL ZELDIN AND YULI ZHANG

CLASS Cofacial polymers

STRUCTURE
$[M(hp)O]_n$:



SYNTHESIS Preparation of $[Si(hp)O]_n$ and $[Ge(hp)O]_n$.[1]



$[hpH_2]$

$$hpH_2 + MCl_4 \longrightarrow M(hp)Cl_2$$

$$M(hp)Cl_2 \xrightarrow{\text{Hydrolysis}} M(hp)(OH)_2$$

$$M(hp)(OH)_2 \xrightarrow[\text{Vacuum}]{\text{Heat}} M(hp)(O)_n$$

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Infrared spectroscopy[1]

COMPOUND	IR SPECTRAL DATA (cm^{-1})*
$[Si(hp)O]_n$	3092(vw), 3042(w), 1684(m), 1640(s), 1589(vs), 1553(m/s), 1437(s), 1323(m), 1293(m), 1264(m), 1209(m), 1170(w), 1160, 1152(w), 1105(s), 990(m-s), 909(w), 811(vs), 771(m), 744(w), 710(vs), 703(vs), 681(m), 503(m), 485(m), 406(w/m)
$[Ge(hp)O]_n$	3080(vw), 3040(vw), 1672(m), 1629(s), 1603(vs), 1582(vs), 1549(s), 1433(vs), 1318(s), 1290(w), 1256(m), 1206(m), 1190(vw), 1153(w), 1110(vs), 1004(vw), 900(m), 808(vs), 768(w), 734(vw), 700(vs), 678(w), 485(vw), 472(vw)

*Peaks not readily assigned to M(hp) moiety; s = strong, m = medium, w = weak, v = very.

Densities[1]

POLYMER	*y*	DENSITY ($g\ cm^{-3}$)
$[Si(hp)O]_n$	Nondoped	1.63
$[Ge(hp)O]_n$	Nondoped	1.62

REFERENCE

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Silk protein

STEPHEN A. FOSSEY AND DAVID L. KAPLAN

ALTERNATIVE NAMES Silk, fibroin, spidroin

CLASS Polypeptides and protein

STRUCTURE

$$[-NH-\underset{}{\overset{R}{\overset{|}{C}}}H-COO-]_n$$

(R = H, CH_3, or CH_2OH in crystalline domains)

MAJOR APPLICATIONS Clothing, sutures.

PROPERTIES OF SPECIAL INTEREST Natural fibers with high strength and compliance, high energy absorption before failure, durable fibers with high luster, resistant to proteolysis.

PREPARATIVE TECHNIQUES Type of polymerization: biosynthesis (enzymatic), ambient conditions of temperature and pressure.

PROPERTY	UNITS	CONDITIONS	VALUES	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	~64	–
Tacticity	–	Enzymatic polymerization (all L-amino acids)	100% isotactic	–
Degree of branching	%	Linear protein	None	–
Molecular weight	$g\,mol^{-1}$	–	350,000	(1)
Polydispersity index M_w/M_n	–	Monodisperse due to genetic controls	1.0	–
Morphology in multiphase systems	–	Crystalline blocks with amorphous blocks	Block copolymers	(2)
IR (characteristic absorption frequencies)	cm^{-1}	Amide I Amide II Amide III	1,624 1,522 1,258	(3)
UV (characteristic absorption frequencies)	nm	Tyrosine	280	–
NMR	–	^{13}C NMR ^{2}H NMR ^{15}N NMR		(4, 5) (6) (7)

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PROPERTY	UNITS	CONDITIONS	VALUES	REFERENCE
Coefficient of linear thermal expansion	K^{-1}	For dry film range 50–150°C	0.461×10^{-4}	(8)
Solvents	$0.06\,g\,ml^{-1}$ silkworm silk in 9.3 M LiBr in H2O $0.28\,g\,mol^{-1}$ silkworm silk in 75% wt/wt $Ca(NO_3)_2$/MeOH $0.1\,g\,ml^{-1}$ *N. clavipes* dragline silk in hexafluoroisopropanol (highest reported solubility, but probably higher)			(9) (10) (11)
Nonsolvents	Methanol, ethanol, nonpolar hydrocarbons			(12)
Second viral coefficient	$mol\,cm^3\,g^{-2}$	*Nephila clavipes* spider dragline silk in hexafluoroisopropanol with 10 mM trifluoroacetic acid	3.0×10^{-3}	(13)
Mark-Houwink parameters: K and a	$K = ml\,g^{-1}$ a = None	–	$K = 1.8 \times 10^{-4}$ $a = 0.81$	(13)

Lattice and unit cell dimensions

	Lattice	Unit cell dimensions (nm)				Reference
		a	*b*	*c* (chain axis)		
Silk I	Orthorhombic	0.896	1.126	0.646	4 residues	(14)
Silk II	Orthorhombic	0.944	0.920	0.695	4 residues	(15, 16)
Silk III	Hexagonal	0.456	0.456	0.867	3 residues	(17)

PROPERTY	UNITS	CONDITIONS	VALUES	REFERENCE
Degree of crystallinity	%	Silkworm silk Spider silk	~38–66 ~20–45	(18) (19)
Density (crystalline)	$g\,cm^{-3}$	Fiber in benzene In water	1.351 1.421	(20)
Crystallite size (typical)	nm	Silkworm silk *N. clavipes* dragline	1.0–2.5 $2 \times 5 \times 7$	(18) (21)
Glass transition temperature T_g	K	0% RH at 23–26°C, absorbed moisture = 0 g/100 g silk 75% RH at 23-26°C, absorbed moisture = 21 g/100 g silk	451 312	(22)
Melting point	–	Degrades prior to melting		
Mesomeric transition	–	Room temperature	Lyotropic	(23)

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PROPERTY	UNITS	CONDITIONS	VALUES	REFERENCE
Heat capacity	$J\,g^{-1}\,K^{-1}$	Specific heat	1.38	(24)
Polymers with which compatible	—	—	Nylon	—
Thermal stability	—	Spider dragline silk (*N. clavipes*)	5% weight loss to 234°C	(25)
		Silkworm silk (*B. mori*)	5% weight loss to 250°C	(26)
Tensile strength	MPa	Silkworm (*Bombyx mori*) silk	513	(24)
Maximum extensibility	%	Silkworm (*Bombyx mori*) silk	23.4	(24)
Work to rupture	MPa	Silkworm (*Bombyx mori*) silk	80.6	(24)
Tensile modulus	MPa	Silkworm (*Bombyx mori*) silk	9,860	(24)
Yield stress	MPa	Silkworm (*Bombyx mori*) silk	211	(24)
Yield strain	%	Silkworm (*Bombyx mori*) silk	3.3	(24)
Storage modulus	MPa	Silkworm (*Bombyx mori*) silk, for $80°C < T < 160°C$	70,000	(27)
Loss modulus	MPa	Silkworm (*Bombyx mori*) silk, for $80°C < T < 160°C$	1,600	(27)

Spider dragline silks

	Tensile strength (GPa)	Initial tensile modulus (GPa)	Ultimate elongation (%)	Shear modulus (GPa)	Transverse comp. modulus (GPa)	Reference
Nephila clavipes	1.1	22	9	—	—	(25)
Nephila clavipes	0.85	12.7	20	3.58	0.58	(28)
Argiope aurantia	0.5-1.3	6-24	18.3–21.5	—	—	(29)
Araneus sericatus	1.0	10	30	—	—	(29)

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PROPERTY	UNITS	CONDITIONS	VALUES	REFERENCE
Index of refraction n	—	Parallel to fiber	1.591	(24)
		Perpendicular to fiber	1.538	(24)
Piezoelectric coefficient	pN/C	$1/d'_{14}$	3.3	(30)
Speed of sound	m s^{-1}	—	540	(31)
Biodegradability	Ubiquitous microorganisms, proteases, soil, water			
Maximum use temperature	K	*N. clavipes* dragline silk	443	(25)
		B. mori silkworm silk	443	(26)
Decomposition temperature	K	*N. clavipes* dragline silk	507	(25)
		B. mori silkworm silk	523	(26)
Water absorption	Some spider silks supercontract ~50% in water			(32)
Scission	—	UV light		(33)
Important patents				(34)

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Starch

W. BROOKE ZHAO

CLASS Carbohydrate polymers

STRUCTURE See *Amylose* and *Amylopectin* constituents in the entries by the same names in this handbook.

MAJOR APPLICATIONS Food industries, adhesives, paper and textile industries, chemicals, reinforcement in rubber, polyelectrolyte applications, and biodegradable blends and composites.

PROPERTIES OF SPECIAL INTEREST The α-glucopyranose linkage in starch is more susceptible to hydrolysis or enzyme attack than the β-glucopyranose linkage in cellulose, thus making starch more attractive for biodegradation applications than cellulose.

PREPARATIVE TECHNIQUE Commercial starch is produced mainly from maize. Limited amounts of starch are also produced from potatoes and wheat. Other plant sources include rice, tapioca, sago, arrowroot, etc.

PRODUCTION LEVEL AND COST The total production level is more than 230 billion pounds annually. The price of commercial starch is around $0.15–0.18 per pound.

PROPERTIES	UNITS	CONDITIONS	VALUES	REFERENCE
Size of granules	μm	Source and Shape		(1)
		Corn, polygonal or round	5–25 (avg. 15)	
		Maize, polygonal or round	5–25 (avg. 15)	
		Potato, oval or egg-shaped	15–100	
		Rice, polygonal	3–8	
		Tapioca, rounded, truncated at one end	20, 15–25	
		Wheat, flat, round, or elliptical	2–10, 20-35	
Gelatinization temperature	K	Source		(1)
		Corn	335–345	
		Sorghum	341.5–348	
		Wheat	325–336	
		Rice	334–350.5	
		Waxy maize	336–345	
		Tapioca	331.5–343	
		Potato	329–339	

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PROPERTIES	UNITS	CONDITIONS	VALUES		REFERENCE
Enthalpy of gelatinization ($-\Delta H_G$)	$kJ\,mol^{-1}$	Corn, A (X-ray pattern)	2.8–3.3		(2)
		Wheat, A (X-ray pattern)	2.0		
		Rice, A (X-ray pattern)	2.3–2.6		
		Dasheen, A (X-ray pattern)	2.9		
		Waxy maize, A (X-ray pattern)	3.2		
		Compacted corn, A (X-ray pattern)	1.5		
		High amylose corn, B (X-ray pattern)	4.5		
		Potato, B (X-ray pattern)	3.0		
		Arrowroot, C (X-ray pattern)	3.1		
		Tapioca, C (X-ray pattern)	2.7		
Density	$g\,cm^{-3}$	Maize			
		Pycnometric	1.637		(3)
		Buoyant	1.50		(3)
		Potato			
		Pycnometric	1.617		(3)
		Perfect evacuation	1.594		(3)
		Wheat			
		Pycnometric	1.650		(4)
		Corn	1.5		(5)
		Sorghum	1.5		(5)
		Rice, nonwaxy			
		Xylene displacement	1.49–1.51		(6)
		Rice, waxy			
		Xylene displacement	1.48–1.50		(6)
		Perfect evacuation	1.646		(4)
Molecular weight (of repeat unit)	$g\,mol^{-1}$	Exclusion chromatography	M_n	M_w	(7)
		Regular dent corn starch	2.14×10^5	1.45×10^7	
		Waxy maize	1.48×10^5	2.18×10^7	
		Amylomaize (70–75% amylose)	4.8×10^4	3.96×10^6	
		Amylomaize (52% amylose)	5.4×10^4	5.75×10^6	
Polydispersity index (M_w/M_n)	—	Regular dent corn starch	68		(7)
		Waxy maize	147		(7)
		Amylomaize (70–75% amylose)	82		(7)
		Amylomaize (52% amylose) in DMSO solution, GPC	106		(7)
		$M_w = 7.11 \times 10^6$; $M_n = 1.35 \times 10^6$	5.27		(8)

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PROPERTIES	UNITS	CONDITIONS	VALUES	REFERENCE
Polymorphs	–	Cereal grain starches, such as from maize, wheat, and rice	A	(3)
		Tuber, fruit, and stem starches, such as from potato, sago, and banana	B	
		Mixture of A- and B-type crystallites	C	
NMR (^{13}C chemical shift)	ppm	Solid state CP/MAS		(9)
		A polymorph	102.3 (0.3), 101.5(0.4), 100.3(0.4) (t) (C-1)	
			62.8(0.2) (C-6)	
			101.4(0.4), (C-1), 100.4(0.4) (d) (C-1)	
		B polymorph	62.1(0.2) (C-6)	
Glass transition temperature T_g	K	Corn starch	496	(10)
Heat capacity increment at T_g (ΔC_p)	$kJ\,K^{-1}\,mol^{-1}$	Corn starch	0.47	(10)
Melting temperature T_m	K	A + B polymorphs	530	(10)
		Maize, A	460	(3)
		Wheat, A	454	(3)
		Waxy maize, A	470	(3)
		Potato, B	441	(3)
Enthalpy of melting ΔH_m	$kJ\,mol^{-1}$	Maize, A	57.7	(3)
		Wheat, A	52.7	
		Waxy maize, A	61.1	
		Potato, B	59.8	
Heat of hydration	$J\,g^{-1}$	Potato	116.7	(3)
		Wheat	105.4	
		Maize	103.3	
		Rice	101.7	
Activation energy for hydration	$kJ\,g^{-1}$	Wheat starch Dielectric absorption	42.3	(3)
Flory-Huggins interaction parameter χ	–	–	0.5	(10)
Birefringence	–	In water and alcohol	0.0131–0.0139	(3)
		In aldehydes	0.0135–0.0143	
		In hydrophobic liquids	0.0134–0.0135	
Refractive indexes	–	Potato starch, 25°C, $\lambda = 589$ nm	1.523, 1.535	(3)

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PROPERTIES	UNITS	CONDITIONS	VALUES	REFERENCE
Surface area	$m^2\,g^{-1}$	Dasheen		(3)
		N_2 adsorption	2.62	
		Photomicrographic	2.64	
		Corn		
		N_2 adsorption	0.70	
		Photomicrographic	0.48	
		Tapioca		
		N_2 adsorption	0.28	
		Photomicrographic	0.25	
		Potato		
		N_2 adsorption	0.11	
		Photomicrographic	0.15	
Surface tension	dynes cm^{-1}	Corn starch	39	(11)
Tensile strength	MPa ($\times 10^{-3}$)	Waxy maize	34.9	(12)
		Tapioca	44.0	
		Potato	44.2	
		Wheat	46.3	
		Corn (A)	46.1	
		Corn (B)	46.7	
		High-amylose corn	50.3	
		15-F acid-modified	44.7	
		34-F acid modified	44.5	
		50-F acid modified	49.4	
		71-F acid modified	45.7	
		89-F acid modified	45.8	
		Hypochlorite-oxidized	48.7	
		Hypocholorite-oxidized	45.0	
		0.05-D.S. hydroxyethyl corn	47.4	
		0.05-D.S. hydroxyethyl, acid-modified corn	41.8	
Elongation at break	%	Waxy maize	1.7	(12)
		Tapioca	3.4	
		Potato	3.1	
		Wheat	2.9	
		Corn (A)	2.5	
		Corn (B)	3.2	
		High-amylose corn	2.5	
		15-F acid-modified	2.7	
		34-F acid modified	2.6	
		50-F acid modified	2.7	
		71-F acid modified	2.9	
		89-F acid modified	2.2	
		Hypochlorite-oxidized	3.0	
		Hypocholorite-oxidized	2.3	
		0.05-D.S. hydroxyethyl corn	2.5	

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PROPERTIES	UNITS	CONDITIONS	VALUES	REFERENCE
Elongation at break	%	0.05-D.S. hydroxyethyl, acid-modified corn	2.6	
Biodegradation	—	Films obtained after extrusion of native potato starch and glycerol		(13)
		Enzymatic test	100% weight loss after 24 h	
		Head-space test	100% CO_2 evolution after 50 days	
		Compost test	100% weight loss after 49 days	

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Styrene-acrylonitrile

SHUHONG WANG

ACRONYM, TRADE NAMES SAN, Lustran® (Monsanto), Tyril® (Dow)

CLASS Chemical copolymers

STRUCTURE $-[\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2]_m-[\underset{\displaystyle CN}{\underset{|}{CH}}-CH_2]_n-$

TYPICAL COMONOMERS Styrene, acrylonitrile

POLYMERIZATION Emulsion, suspension, and continuous processes.

MAJOR APPLICATIONS Incorporated in acrylonitrile-butadiene-styrene (ABS) (≥80%). Appliances, housewares, packing materials, automotive features, industrial applications, and custom molding products.

PROPERTIES OF SPECIAL INTEREST Rigidity, resistance to heat and chemicals (acids, alkalies, fat, grease, oil, gasoline, alcohol, and some solvents), and high optical clarity.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\ cm^{-3}$	–	1.07–1.09	(1)
Glass transition temperature T_g	K	20 mol% acrylonitrile (AN)	~376	(2)
		40 mol% AN	~381	
		50 mol% AN	~383	
		75 mol% AN	~382	
Rockwell Hardness	–	Lustran-35, ASTM D785	83	(3)
		Tyril-880, ASTM D785	80	(4)
Tensile strength	MPa	5.5% AN	42.27	(2)
		9.8% AN	54.61	(2)
		14.0% AN	57.37	(2)
		21.0% AN	63.68	(2)
		27.0% AN	72.47	(2)
		Lustran-35, ASTM D638	79.4	(3)
		Tyril-880, ASTM D638	82.1	(4)
Elongation	%	5.5% AN	1.6	(2)
		9.8% AN	2.1	(2)
		14.0% AN	2.2	(2)
		21.0% AN	2.5	(2)
		27.0% AN	3.2	(2)
		Lustran-35, ASTM D638	3.0	(3)
		Tyril-880, ASTM D638	3.0	(4)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Impact strength	J m^{-1}	5.5% AN, notch	26.6	(2)
		9.8% AN, notch	26.0	
		14.0% AN, notch	27.1	
		21.0% AN, notch	27.1	
		27.0% AN, notch	27.1	
Izod impact strength	J m^{-1}	Lustran-35, ASTM D256	24.0	(3)
		Tyril-880, ASTM D256	26.7	(4)
Heat distortion	K	5.5% AN	345	(2)
		9.8% AN	355	
		14.0% AN	357	
		21.0% AN	361	
		27.0% AN	361	
Deflection temperature	K	Lustran-35, ASTM D648	377.6	(3)
		Tyril-880, ASTM D648	376.5	(4)
Vicat softening point	K	Lustran-35, ASTM D1525	384	(3)
		Tyril-880, ASTM D1525	384	(4)
Melt-flow rate	g (10 min)$^{-1}$	Lustran-35, ASTM D1238	7.0	(3)
		Tyril-880, ASTM D1238	3.0	(4)
Coefficient of linear thermal expansion	cm (cm K)$^{-1}$	Lustran-35, ASTM D696	6.8×10^{-5}	(3)
		Tyril-880, ASTM D696	6.6×10^{-5}	(4)
Flammability	mm s^{-1}	Tyril-880, ASTM D635	0.333	(4)
Specific heat	J g^{-1} K^{-1}	Tyril-880, Dow Test	1.30	(4)
Dielectric constant	–	Tyril-880, ASTM D150	3.18	(4)
Dissipation factor	kHz	Tyril-880, ASTM D150	0.007	(4)
Index of refraction n_D	–	Lustran-35, ASTM D542	1.57	(3)
		Tyril-880, ASTM D542	1.57	(4)
Water absorption	%	Lustran-35, ASTM D570(24 h)	0.25	(3)
		Tyril-880, ASTM D570 (24 h)	0.35	(4)
Solution viscosity	mPa s	5.5% AN, 10% in MEK	11.1	(2)
		9.8% AN, 10% in MEK	10.7	
		14.0% AN, 10% in MEK	13.0	
		21.0% AN, 10% in MEK	16.5	
		27.0% AN, 10% in MEK	25.7	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Specific gravity	—	Lustran-35, ASTM D792	1.07	(3)
		Tyril-880, ASTM D792	1.08	(4)
Mold shrinkage	cm cm^{-1}	Lustran-35	0.003–0.004	(3)
		Tyril-880	0.003–0.007	(4)
Thermal conductivity	W m^{-1} K^{-1}	33% glass fiber	0.28	(5)
Theta temperature θ	K	51% AN, ethyl acetate	316.2	(6)

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Styrene-butadiene elastomers

SHUHONG WANG

ACRONYMS, TRADE NAMES SBR, SB; Ameripol®, Synpol® (Ameripol Synpol); Copo®, Carbomix® (DSM Copolymer); Darex® (W.R. Grace); Duradene®, Srereon® (Firestone); Gentro® (Diversitech General); Humex® (Hules Mexicanos, S.A.); JSR (Japan Synthetic Rubber Co.); NIPOL (Nippon Zeon Co.); Plioflex®, Pliolite® (Goodyear Tire & Rubber); Polysar SS®, Polysar S® (Bayer AG); Solprene® (Negromex, S.A.); Tylac® (Reichhold Chemicals)

CLASS Chemical copolymers

STRUCTURE $-[CH_2-CH{=}CH-CH_2]_m-[CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}]_n-$

TYPICAL COMONOMERS Styrene and butadiene.

MAJOR APPLICATIONS Tires (~75%), shoes and other footware, mechanical goods, sponge and foamed products, waterproofed materials, hose, belting, adhesives, etc.

PROPERTIES OF SPECIAL INTEREST Standard emulsion SBR is a general purpose rubber. Most widely used synthetic rubber in the world. Better tire tread-wear and aging properties than natural rubber. Good abrasion resistance and crack initiation resistance. Poor in tack and heat build-up. Physical properties are poor without reinforcing fillers. Solution SBR is a speciality rubber and more expensive than emulsion SBR. Solution SBR with high vinyl and styrene levels is used in high performance tire treads to improve wet traction. Also used as impact modifier in plastics and as thermoplastic elastomers.

EMULSION POLYMERIZATION Used for standard SBR. Monomer is emulsified in water with emulsifying agents. Polymerization is initiated by either decomposition of a peroxide or a peroxydisulfate. Hot SBR is initiated by free radicals generated by thermal decomposition of initiators at 50°C or higher. Cold SBR is initiated by oxidation-reduction reactions (redox) at temperatures as low as −40°C. Styrene content normally is 23%. Copolymer is randomly distributed. Structure of butadiene contents is about 18% *cis*-1,4, 65% *trans*-1,4, and 15–20% vinyl.

Typical polymerization conditions

Type	Hot	Cold
Monomer ratio (S:B)	71:9	71:29
Water:monomer	2:1	2:1
Emulsifier	Fatty acid	Rosin acid
Coagulation	Acid/amine	Acid/amine
Temperature (°C)	50	5
Conversion (%)	72	60–65
Styrene content	24	24
Mooney at 100°C	48	46–58

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Commercial grades (IISRP* numbering system)

1,000	Hot SBR
1,500	Cold SBR
1,600	Cold SBR black masterbatch with 14 or less phr oil
1,700	Cold SBR oil-masterbatch
1,800	Cold oil-black masterbatch with more than 14 phr oil
1,900	Miscellaneous resin rubber masterbatches
2,000	Hot latexes
2,100	Cold latexes

*International Institute of Synthetic Rubber Products.

SOLUTION POLYMERIZATION Solution SBR typically made in hydrocarbon solution with alkyl lithium-based initiator. In this stereo-specific catalyst system, in principle, every polymer molecule remains live until a deactivator or some other agent capable of reacting with the anion intervenes. Able to control molecular weight, molecular weight distribution, and branching. Able to make random and block copolymers with designed chain sequence. Able to make copolymer with controlled styrene content. Able to control the butadiene structure of vinyl/*cis*/*trans*. Higher purity due to no addition of soap.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\ cm^{-3}$	Emulsion SBR, 23–25% styrene	0.93	(1)
		Solution SBR, 8–77% vinyl, 13–27% styrene	0.92–0.95	(2)
Mark-Houwink parameters: K and a	$K = ml\ g^{-1}$ a = None	Emulsion hot SBR measured in toluene at 30°C	$K = 5.4 \times 10^{-4}$ $a = 0.66$	(3)
Refractive index	—	Solution SBR, block copolymer, 30% styrene	1.53	(4)
Service temperature (maximum)	K	Emulsion SBR , 23% styrene	343	(5)
		Solution SBR, block copolymer, S:B = 1:100	338	
Solubility parameter	$(MPa)^{1/2}$	Emulsion SBR, 15% styrene	17.39	(1)
Thermal conductivity	$W\ m^{-1}\ K^{-1}$	33% carbon black loaded	0.300	(1)
Theta temperature θ	K	Emulsion SBR, 23.9% styrene in methyl *n*-propyl ketone	294	(1)
		Emulsion SBR, 23.9% styrene in methyl isobutyl ketone	319	
		Emulsion SBR, 25% styrene in *n*-octane	294	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Glass transition temperature T_g	K	Emulsion SBR, 23% styrene	221	(3)
		Emulsion SBR, 36% styrene	235	(3)
		Emulsion SBR 53% styrene	259	(3)
		Emulsion SBR, 75% styrene	286	(3)
		Solution SBR, block copolymer, S:B = 1:100	203, 363	(3)
		Solution SBR, 8–77% vinyl, 13–27% styrene	238–266	(2)
		Emulsion SBR at 50°C	$[(-85 + 135S)/(1 - 0.5S)] + 273^*$	(6)
		Emulsion SBR at 5°C	$[(-78 + 128S)/(1 - 0.5S)] + 273^*$	(6)
		Solution SBR, assume T_g of styrene as 100°C, T_g of polybutadiene as −100°C, and T_g of all-vinyl polybutadiene as 0°C	$[1/(0.00578 - 0.0031S - 0.00212V + 0.00212VS)] + 273^*$	(6)
Tensile strength	MPa	Unfilled vulcanizate, emulsion hot SBR, 23–25% styrene	1.4–2.8	(1)
		1006 in ASTM 3185 1A (see also tables below)	21.4	(7)
		1500 in ASTM 3185 1A (see also tables below)	23.5	(7)
		1605 in ASTM 3186 (see also tables below)	19.3	(7)
		1721 in ASTM 3185 2B (see also tables below)	19.0	(7)
		1805 in ASTM 3186 (see also tables below)	18.6	(7)
Elongation	%	Unfilled vulcanizate, emulsion hot SBR, 23–25% styrene	450–600	(1)
		1006 in ASTM 3185 1A (see also tables below)	325	(7)
		1500 in ASTM 3185 1A (see also tables below)	450	(7)
		1605 in ASTM 3186 (see also tables below)	350	(7)
		1721 in ASTM 3185 2B (see also tables below)	525	(7)
		1805 in ASTM 3186 (see also tables below)	350	(7)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Modulus	MPa	Unfilled vulcanite, emulsion hot SBR, 23–25% styrene	1–2	(1)
		1006 in ASTM 3185 1A (see also tables below)	13.8–17.9	(7)
		1500 in ASTM 3185 1A (see also tables below)	10.4–14.5	(7)
		1605 in ASTM 3186 (see also tables below)	13.5–17.6	(7)
		1721 in ASTM 3185 2B (see also tables below)	6.2–10.4	(7)
		1805 in ASTM 3186 (see also tables below)	9.0–13.1	(7)

*S = wt. fraction of styrene in the polymer. V = (% vinyl in total polymer ×100)/(% butadiene in polymer).

Conditions

SBR Type	Styrene	Mooney	Carbon black	phr	Oil	phr
1006A	23.5	49	–	–	–	–
1500	23.5	52	–	–	–	–
1605	23.5	62	N550	50	–	–
1721	23.5	55	–	–	Aromatic	37.5
1805	23.5	58	N330	75	Naphthenic	37.5

SBR test compounds

ASTM	Polymer	Furnace black	Stearic acid	Zinc oxide	Sulfur	TBBS
3185 1A	100 phr	50	1	3	1.75	1
3185 2B	137.5 phr	68.75	1	3	1.75	1.38
3186	162 phr	–	1.5	3	1.75	1.25

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Styrene-methylmethacrylate copolymer

SHUHONG WANG

ACRONYM SMMA

CLASS Chemical copolymers

STRUCTURE

$$-[CH_2-CH(C_6H_5)]_m-[CH_2-C(CH_3)(COOCH_3)]_n-$$

TYPICAL COMONOMERS Styrene and methylmethacrylate.

MAJOR APPLICATIONS Blends with other polymers to produce a variety of products. Blends normally have both transparency and impact resistance and perform well in appliance and food-packing applications.

PROPERTIES OF SPECIAL INTEREST Properties fall between those of the individual homopolymers. Better weatherability and solvent resistance compared to polystyrene homopolymer.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Tensile strength	MPa	ASTM D638		(1)
		P-205 UVA extrusion grade	68.2	
		NAS injection-molding grade	57.2	
Tensile elongation	%	ASTM D638		(1)
		P-205 UVA extrusion grade	5.0	
		NAS injection-molding grade	2.0	
Tensile modulus	MPa	ASTM D638		(1)
		P-205 UVA extrusion grade	3,300	
		NAS injection-molding grade	3,500	
Flexural strength	MPa	ASTM D790		(1)
		P-205 UVA extrusion grade	116	
		NAS injection-molding grade	103	
Flexural modulus	MPa	ASTM D790		(1)
		P-205 UVA extrusion grade	3,300	
		NAS injection-molding grade	3,500	
Izod impact strength	$J\ m^{-1}$	ASTM D256		(1)
		P-205 UVA extrusion grade	20	
		NAS injection-molding grade	20	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Specific gravity	–	ASTM D792		(1)
		P-205 UVA extrusion grade	1.13	
		NAS injection-molding grade	1.09	
Rockwell hardness	–	ASTM D785		(1)
		P-205 UVA extrusion grade	80	
		NAS injection-molding grade	64	
Deflection temperature	K	ASTM D648		(1)
		P-205 UVA extrusion grade	372	
		NAS injection-molding grade	371	
Water absorption	%	ASTM D570, 24 h		(1)
		P-205 UVA extrusion grade	0.17	
		NAS injection-molding grade	0.15	
Light transmission	%	P-205 UVA extrusion grade	90	(1)
		NAS injection-molding grade	90	
Haze	%	P-205 UVA extrusion grade	2	(1)
Index of refraction n_D	–	ASTM D542		(1)
		P-205 UVA extrusion grade	1.53	
		NAS injection-molding grade	1.56	
Melt flow rate	g (10 min)$^{-1}$	ASTM D1238		(1)
		P-205 UVA extrusion grade, 190°C/10 kg	0.2	
		NAS injection-molding grade, 190°C/10 kg	4.3	
		P-205 UVA extrusion grade, 230°C/3.8 kg	0.7	
		P-205 UVA extrusion grade, 230°C/1.2 kg	0.13	
Theta temperature θ	K	29.3% styrene, $M_n = 4.7$–59.2		(2)
		2-Ethoxy ethanol	313.2	
		Cyclohexanol	341.2	
		56.2% styrene, $M_n = 3.4$–50		
		2-Ethoxy ethanol	331.6	
		Cyclohexanol	334.5	
		70.2% styrene, $M_n = 4.0$–43		
		2-Ethoxy ethanol	346.8	
		Cyclohexanol	336.2	
		76.3% styrene		
		Benzene/*n*-hexane = 44/56	293.2	
		Benzene/isopropanol = 57/43	293.2	
		n-Hexane/3-methyl butanone = 40/60	293.2	
		58.1% styrene		
		Benzene/*n*-hexane = 51/49	293.2	
		Benzene/isopropanol = 51/49	293.2	
		n-Hexane/3-methyl butanone = 34/66	293.2	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Theta temperature θ	K	42.3% styrene		
		Benzene/*n*-hexane = 59/41	293.2	
		Benzene/isopropanol = 48/52	293.2	
		n-Hexane/3-methyl butanone = 29/71	293.2	
		26.1% styrene		
		Benzene/*n*-hexane = 62/38	293.2	
		Benzene/isopropanol = 41/59	293.2	
		n-Hexane/3-methyl butanone = 24/76	293.2	

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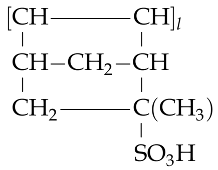
Sulfo-ethylene-propylene-diene monomer ionomers

RUSKIN LONGWORTH

ALTERNATIVE NAME, TRADE NAME Sulfo-EPDM ionomers, Vistalon® derivative (Exxon Chemical Co.)

CLASS Chemical copolymers; EPDM rubber derivatives

STRUCTURE[1] $-(CH_2-CH_2)_n-(CH_2-CH(CH_3))_m-$



$n + m + l = 100$; $n = 52$; $m = 43$; $l = 5$.

GENERAL INFORMATION These polymers consist of sulfonated derivatives of ethylene-propylene-diene terpolymers. The ionic associations induced by the sulfonate groups are significantly stronger than is the case with the carboxylated products. For a detailed comparison, see reference (2). Even after several years of active development, sustainable commercial uses have not emerged. Thus, these products are no longer being produced even though they are of considerable technical interest.

MAJOR APPLICATIONS Drilling mud additives.

Preparative techniques[1]

Sulfonation of rubber	Acetyl sulfate added to cold solution of rubber in hydrocarbon solvent
Neutralization of sulfo-EPDM	Addition of excess solution of metal acetate in water/methanol solvent
Comonomer	Ethylidene norbornene

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\,mol^{-1}$	–	44	(1)
Tacticity	–	–	Slightly nonrandom	(1)
Molecular weight (of ionomer)	$g\,mol^{-1}$	Mooney viscosity, ML, H8, 373 K	20	(1)

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Solvents	—	Sulfo-EPDM, 273 K	Toluene/methanol (95/5)		(1)
		EPDM, 273 K	Hexane		
Crystalline state properties	EPDM and sulfo-derivatives are amorphous				
Tensile strength	MPa ($\times 10^{-3}$)	(a) Effect of neutralizing ion (base polymer: sulfo-EPDM, 2.7% sulfonic acid; 100% neutralized)			(1)
		Ion: Mg	2.21		
		Co	8.13		
		Pb	11.03		
		Zn	10.20		
		(b) Effect of plasticizer (base polymer: sulfo-EPDM, 3.8% zinc sulfonate)	298 K	343 K	(3)
		Zinc stearate (%): 0	6.76	1.72	
		16	21.0	4.48	
		27	25.2	6.41	
		36	22.4	7.93	
Elongation	%	Effect of neutralizing ion (base polymer: sulfo-EPDM, 2.7% sulfonic acid; 100% neutralized)			(1)
		Ion: Mg	70		
		Co	290		
		Pb	480		
		Zn	400		
Melt viscosity	Pa s ($\times 10^{-3}$)	(a) Effect of cation on melt viscosity (base polymer: sulfo-EPDM, 2.7% sulfonic acid)			(1)
		Ion: Ca	5.32		
		Li	5.15		
		Na	5.06		
		Pb	3.28		
		Zn	1.20		
	$g\,s^{-1}$ ($\times 10^{-3}$)	(b) Effect of stearic acid on melt viscosity (base polymer: sulfo-EPDM, 3.8% zinc sulfonate)	Viscosity as melt index at 463 K, 1.72 kPa		(3)
		Stearic acid (%): 0	<0.1		
		16	0.50		
		27	1.60		
		36	5.00		

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Melt viscosity	$g\,s^{-1}$ ($\times 10^{-3}$)	(c) Effect of zinc stearate on melt viscosity (base polymer: sulfo-EPDM, 3.8% zinc sulfonate)	Viscosity as melt index at 463 K, 1.72 kPa	(3)
		Zinc stearate (%): 0	<0.1	
		16	0.50	
		27	2.3	
		36	6.3	
Water absorption (gain)	%	(a) Base polymer: sulfo-EPDM, 3.8% zinc sulfonate; at 323 K for:		(2)
		24 h	5	
		72 h	7	
		144 h	8	
		310 h	11	
		(b) Plasticized composition: sulfo-EPDM, 3.8% zinc sulfonate plasticized with 36% zinc stearate; at 323 K for:		(3)
		24 h	3.3	
		72 h	4.1	
		144 h	4.9	
		310 h	5.4	
Important patents	O'Farrell, C. P., and G. E. Serniuk. *U.S. Patent* 3,836,511 (1972), assigned to Esso Research and Engineering Co. Canter, N. H., and D. J. Buckley, Sr. *U.S. Patent* 3,847,854 (1974), assigned to Esso Research and Engineering Co. Canter, N. H. *U.S. Patent* 3,642,728 (1974), assigned to Esso Research and Engineering Co.			
Cost and availability	—	—	Unavailable	—

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Syndiotactic polystyrene

JUNZO MASAMOTO AND TAKASHI IWAMOTO

ACRONYM, TRADE NAME SPS, XAREC (Idemitsu Petro Chemicals)

CLASS Vinyl polymers

STRUCTURE $[-CH_2CH(C_6H_5)]$

MAJOR APPLICATIONS Thermoplastics as an engineering plastic, usually reinforced with glass fiber, and used for automobile parts, electrical and electronic parts. SPS neat resin film is available for sheet and tape.

PROPERTIES OF SPECIAL INTEREST Crystalline engineering plastics starting from a commodity monomeric material of styrene. Quite different properties compared to conventional amorphous polystyrene. High melting point (463 K) and good solvent resistance. Excellent electrical properties with low dielectric loss. High heat deflection temperature, low water absorption and hydrolytic resistance. Excellent dimensional precision during injection molding because of equal density of amorphous and crystalline parts.

PREPARATIVE TECHNIQUE Metallocene polymerization: Combination of $Cp^{*}Ti(OiPr)_3$ [pentamethyl cyclopentadienyl titanium triisopropoxide] and MAO [methyl almoxane], or combination of $Cp^{*}Ti(Me)_3$ [pentamethyl cyclopentadienyl titanium trimethyl] and $B(C_6F_5)_3$ [tris-(pentafluorophenyl) borane] usually polymerized around 70–90°C, under bulk polymerization conditions.[1–3]

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Molecular weight (of repeat unit)	$g\ mol^{-1}$	—	104	—
Tacticity (stereo regularity)	%, pentad, syndiotacticity	Metallocene polymerization	>98	(4)
Typical molecular weight range of polymer M_w	$g\ mol^{-1}$	Metallocene polymerization: combination of $Cp^{*}Ti(OMe)_3$ [pentamethyl cyclopentadienyl titanium trimethoxide] and MAO [methyl almoxane], or combination of $Cp^{*}Ti(Me)_3$ [pentamethyl cyclopentadienyl titanium trimethyl] and $B(C_6F_5)_3$ [tris-(pentafluorophenyl)borane] usually polymerized around 70–90°C, under bulk polymerization conditions	2–5 ($\times 10^5$)	(1–3)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Typical polydipersity index (M_w/M_n)	–	–	2	(1–3)
IR (characteristic absorption frequencies)	cm^{-1}	Planar zigzag conformation (T4) Helex conformation (TTGG)	1,224 935	(5)
NMR	The 67.8 MHz ^{13}C-NMR: 1,2,4-trichrolobenzene at 130°C with JNMGX-270 spectrometer The 270 MHz ^{1}H-NMR: 1,2,4-trichrolobenzene at 130°C with JNMGX-270 spectrometer			(4)
Thermal expansion coefficients	K^{-1}	Neat SPS 30% glass fiber filled SPS	9.2×10^{-5} 2.5×10^{-5}	(6)
Solvent	–	130°C	Trichlorobenzene	(4)
Nonsolvents	–	At its boiling point	Methanol, methyl ethyl ketone	(4)

Unit cell dimensions

	Lattice	Polymer chain per unit cell	Cell dimension (Å)			Cell angles			Reference
			a	*b*	c (chain axis)	α	β	γ	
α	Hexagonal	18	26.25	–	5.045	–	–	–	(7)
β	Orthorhombic	4	8.81	28.82	5.06	–	–	–	(8)
γ	Monoclinic	2	–	–	–	–	–	–	(9)
δ	Monoclinic	2	17.58	13.26	7.71	–	–	121.2	(9)

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Space group	–	–	α P62C β Pbnm δ $P2_1/a$	(7) (8) (9)
Chain conformation	–	α β γ δ	(T_4) (T_4) $(TTGG)_2$ $(TTGG)_2$	(7) (8) (9) (9)
Degree of crysatallinity	%	Quenched from 320°C in ice water Injection molded sample at the mold temperature of 140°C	~0 50	(10)
Heat of fusion	$kJ\,mol^{-1}$ $mJ\,mg^{-1}$	–	5.8 53	(11) (10)

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Density	$g\,cm^{-3}$	Neat SPS	1.05	(12)
		α crystal	1.033	(7)
		β crystal	1.08	(8)
		δ crystal (molecular compound with toluene)	1.11	(9)
Polymorphs	—	—	α crystal (T_4)	(7)
			β crystal (T_4)	(8)
			γ crystal $(TTGG)_2$	(9)
			δ crystal $(TTGG)_2$	(9)
Glass transition temperature	K	—	373	(1)
Melting point	K	DSC, $20°C\,min^{-1}$	543	(2)
Equilibrium melting point	K	Crystallization temperature	548	(13)
		vs. polymer melting point	558	(14)
		Lammela thickness vs. polymer melting point	583	(15)
Mesomeric transition temperature	K	From helix $(TTGG)_2$ to planar zigzag (T_4)	463	(16)
Heat capacity	$kJ\,K^{-1}\,mol^{-1}$	—	0.140	(17)
Deflection temperature	K	Neat SPS, $18.3\,kg\,cm^{-2}$	372	(12)
		30% glass fiber filled SPS, $18.3\,kg\,cm^{-2}$	522	
Polymer with which compatible	—	SPS, $M_w = 680{,}000$	Poly(2,6-dimethyl-1,4-phenyleneoxide)	(18)
Tensile modulus	MPa	Neat SPS	3,440	(12)
		30% glass fiber filled SPS	10,000	
Tensile strength	MPa	Neat SPS	41	(12)
		30% glass fiber filled SPS	121	
Yield stress	MPa	Neat SPS	41	(12)
		30% glass fiber filled SPS	121	
Yield strain	%	Neat SPS	1.0	(12)
		30% glass fiber filled SPS	1.5	
Flexural modulus	MPa	Neat SP	39	(12)
		S30% glass fiber filled SPS	97	

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Flexural strength	MPa	Neat SP	71	(12)
		S30% glass fiber filled SPS	166	
Izod impact	$kJ\,m^{-1}$	Neat SPS	11	(12)
		30% glass fiber filled SPS	96	(19)
Dielectric constant	–	Neat SPS [1 MHz]	2.6	(20)
		30% glass fiber filled SPS	2.9	
Dielectric loss	–	Neat SPS	<0.001	(20)
		30% glass fiber filled SPS	<0.001	
Breakdown strength	$kV\,mm^{-1}$	Neat SPS	66	(21)
		30% glass fiber filled SPS	48	
Resitivity	ohm cm	Neat SPS, ASTM D 257	$>10^{16}$	(6)
		30% glass fiber filled SPS, ASTM D 257	$>10^{16}$	
Maximum use temperature (long term)	K	–	400	(6)
Water absorption	%	Neat SPS, 24 h equilibrium, ASTM D 570	0.04	(6)
		30% glass fiber filled SPS, 24 h equilibrium ASTM D 570	0.05	
Important patent	U.S. Patent 5,502,133 U.S. Patent 4,680,353			
Availability	$kg\,yr^{-1}$	–	5×10^6	–
Suppliers	Idemitsu Petro Chemicals, 3-1-1, Marunouchi, Chiyoda-ku, Tokyo 100, Japan ($5 \times 10^6\ kg\,yr^{-1}$)			

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Vinylidene fluoride–hexafluoropropylene elastomers

RAHUL D. PATIL

ACRONYMS, ALTERNATIVE NAMES, TRADE NAMES Poly(vinylidene fluoride-co-hexafluoropropylene), poly(vdf-hfp), Dai-el, Fluorel, Tecnoflon, Viton[1,2]

CLASS Chemical copolymers; fluoroelastomers

CAS REGISTRY NUMBER [9011-17-0]

STRUCTURE

$$-(CF_2-CH_2)_n-(\overset{CF_3}{\overset{|}{C}}F-CF_2)_m-$$

MAJOR APPLICATIONS Poly(vdf-hfp) is a synthetic, noncrystalline polymer that exhibits elastomeric properties when cross-linked. Known to be chemically inert, it is designed for demanding service applications in hostile environments and commonly used as a sealant in hot and corrosive environments.[1,3]

COMMERCIAL USE Poly(vdf-hfp) has found its niche in industry. Once considered exotic and too expensive, it has proven to be the most cost-effective answer to modern sealing needs. Commonly used as a sealant in hot and corrosive environments.[3]

PROPERTIES OF SPECIAL INTEREST Poly(vdf-hfp) contains approximately 30–40 mol% hexafluoropropylene. When the copolymer contains less than 30 mol% hexafluoropropylene it tends to become nonelastic; at less than 15 mol% the copolymer has thermoplastic properties.[2–7]

Preparative technique[6]

Polymerization type	Emulsion
Process	Batch or continuous
Temperature	80–120°C
Pressure	1.72–10.34 MPa
Comonomers	Vinylidene fluoride and hexafluoropropylene
Initiator	Ammonium persulphate
Catalyst	Sodium bisulphate

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^{19}F NMR*[(8)]

Group	Microstucture sequence†	Peak (ppm)
CF_3	H T X T X	71.4
	T T X T H	75.9
CF_2	T H T H T	91.9
	H H T H T	95.7
	T H T X T	103.7
	T H T T H	114.0
	H T T H H	116.3
	H T T X H	118.9
CF	H T X T H	182.3
	T T X H T	184.9

*In 50% acetone at 30°C.
†H = $-CH_2-$; T = $-CF_2-$; X = $-CF(CF_3)-$.

PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Average molecular weight M_w	g mol^{-1}	–	85,000	(9)
Mooney viscosity	ML 1 + 10	At 121°C	22	(7)
Molar ratio of comonomers	–	Vinylidene fluoride/hexafluoropropylene	3.5	(7)
Total fluorine content	%	Viton A	66	(7)
Specific gravity	g cm^{-1}	Gumstock	1.54–1.88	(1)
		Viton A	1.82	(7)
Solubility parameters	(MPa)$^{1/2}$	Total	17.8	(10)
		Nonpolar	15.3	
		Polar	7.2	
		Hydrogen-bonding	5.3	
Solubility	–	In carbon dioxide, at 100°C and 1,000 bar	Soluble	(9)
		In C_3F_3, at 163°C and 2,750 bar	Soluble	(11)
		In $CClF_3$, at 230°C and 1,500 bar	Soluble	(11)
		In CHF_3, at 30°C and 1,500 bar	Soluble	(11)
Intrinsic viscosity [η]	dl g^{-1}	For various compositions at 30°C in methyl ethyl ketone		(12)
		11 mol% of HFP	1.5	
		16.3 mol% of HFP	1.7	
		22.6 mol% of HFP	1.3	
		27.8 mol% of HFP	1.0	

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PROPERTY	UNITS	CONDITIONS	VALUE		REFERENCE
Parameters for Flory-Rehner equation describing sorption isotherms	—	At 25°C in acetone			(3)
		χ_0	1.596		
		χ_1	−3.319		
		χ_2	1.514		
		K	−0.033		
Glass transition temperatures T_g	K	Mol% of HFP			(12)
		11	240.5		
		16.3	244.0		
		22.6	250.0		
		27.8	255.5		
		33.8	261.3		
		40.7	267.8		
Relaxation processes	K	Mol% of HFP	β process (T_β)	α_L process ($T_{\alpha,L}$)	(13)
		19.2	185.35	256.15	
		−87.8	185.35	257.15	
		24.2	183.65	258.15	
		26.0	183.65	260.15	
		30.3	189.15	266.15	
		34.7	189.15	268.15	
		39.0	192.15	271.15	
		39.2	189.15	271.15	
Change in volume	%	At room temperature after 72 h of immersion in water and various alcohols*			(14)
		Solvent			
		Water	−1		
		Methanol	89		
		Ethanol	0.5		
		n-Propanol	0.7		
		n-Butanol	0.4		
		n-Pentanol	0.1		
		n-Hexanol	0.1		
		n-Heptanol	0.2		
		n-Octanol	0.3		

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PROPERTY	UNITS	CONDITIONS	VALUE	REFERENCE
Change in volume	%	After exposure to methanol at various temperatures*		(14)
		Temperature (K)		
		233.15	172	
		253.15	149	
		273.15	121	
		294.15	84	
		303.15	76	
		308.15	68	
		313.15	58	
		323.15	54	
		328.15	39	
		333.15	16	

* Sample used in reference (14) is Viton A, cross-linked and reinforced with carbon black filler. The description of the cross-linking method is given in detail in the same reference.

Effect on mechanical properties* (14)†

Alcohol	% Alcohol	Tensile strength (MPa)	Elongation (%)	Modulus at 100% elongation (MPa)
None	Original properties	16.8	200	5.7
Methanol	0	15.8	232	5.3
	2	12.1	199	4.5
	5	11.7	219	4.0
	10	8.7	178	3.7
	25	5.3	127	3.9
	50	5.6	116	4.6
	75	4.8	96	—
	100	4.3	87	—
Ethanol	0	15.2	153	9.5
	5	12.7	153	6.3
	10	12.3	153	5.8
	15	12.7	150	7.0
	25	12.3	150	6.2
	50	13.0	158	6.3
	75	12.9	152	6.7
	100	14.6	160	7.1

* After 72 h of immersion in mixtures of methanol/indolene and ethanol/indolene at room temperature.
† Sample used in reference (14) is Viton A, cross-linked and reinforced with carbon black filler. The description of the cross-linking method is given in detail in the same reference.

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Mechanical properties[6]

PROPERTY	UNITS	CONDITIONS	TEMPERATURE (K)	VALUE
Tensile strength at break	MPa	Dry*	350	11.79
		Dry*, after 72 h	478	10.27
		Wet†	298	16.20
		—	343	12.76
		—	373	7.23
Elongation at break	%	Wet†	298	390
		Dry*	350	625
		Dry*, after 72 h	478	615
		—	343	490
		—	373	500
Modulus-300%	MPa	Dry*	350	3.44
		Dry*, after 72 h	478	2.90
		Wet†	298	10.00
		—	343	5.52
		—	373	3.27

* The sample used in the dry tests was compounded with dibasic lead phosphite and cured for one hour at 120–150°C. See reference (6) for details.

† The sample used in the wet tests was compounded with silica and cured for one hour at 120°C. See reference (6) for details.

Thermal degradation[15]

Type of elastomer	Atmosphere	Temperature (K)				Final total yield of *F* (%)
		Initial weight loss	1% weight loss	Intial *F* yield	1% *F* yield	
Viton A	Air	613	668	416	704	54.2
	Nitrogen	543	623	409	730	12.9
Viton A-HV	Air	653	693	468	690	54.7
	Nitrogen	623	683	414	703	13.2
Viton A cross-linked	Air	473	633	493	656	56.2
	Nitrogen	443	593	461	634	28.5

Suppliers

Trade name	Supplier
Viton	DuPont Dow Elastomers, 300 Bellevue Parkway, Suite 300, Wilmington, Delaware 19809, USA
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Poly(methylphenylsilylene)

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Polymer Scientist, W. L. Gore and Associates, Inc., Elkton, Maryland
Ethylene-vinyl acetate copolymer
Ethylene-vinyl alcohol copolymer
Polyacetylene

Yong Yang
Research Chemist, Benjamin Moore and Company, Flanders, New Jersey
Cellulose acetate
Cellulose butyrate
Cellulose nitrate
Ethylcellulose
Hydroxypropylcellulose

Qingwen Wendy Yuan
Project Supervisor, National Starch and Chemical Company, Bridgewater, New Jersey
Poly(epichlorohydrin)
Poly(ethylene oxide)
Poly(propylene oxide)
Poly(tetrahydrofuran)
Poly(trimethylene oxide)

Martel Zeldin
Professor of Chemistry, and Dean of Science and Technology, College of Staten Island, City University of New York
Metallophthalocyanine polymers
Silicon (germanium) oxo hemiporphyrazine polymers

Ruzhi Zhang
Department of Chemistry, University of Cincinnati, Ohio
cis-1,4-Polyisoprene

Yuli Zhang
Research Assistant, Department of Chemistry, College of Staten Island, City University of New York
Metallophthalocyanine polymers
Silicon (germanium) oxo hemiporphyrazine polymers

W. Brooke Zhao
Research Scientist, HMT Technology Corporation, Fremont, California
Amylopectin
Amylose
Gelatin
Nylon 6,12
Starch

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